PB-233 139

TREATMENT OF SULFITE EVAPORATOR CONDENSATES FOR RECOVERY OF VOLATILE COMPONENTS

Kenneth W. Baierl, et al

Institute of Paper Chemistry
Appleton, Wisconsin

December 1973

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

PB 233 139

W 74-09066

TREATMENT OF SULFITE EVAPORATOR CONDENSATES FOR RECOVERY OF VOLATILE COMPONENTS,

Baierl, K~~enneth~~ W., Chang, N~~ai~~ L., Lueck, B~~ernard~~ F., Wiley, A~~verill~~ J., and Holm, R~~obert~~ A.

EPA Program Element 1B2037

~~The~~ Institute of Paper Chemistry, Appleton, Wisconsin, Division of Industrial and Environmental Systems.

Grant S801207

Type of Report and Period Covered

Sponsoring Organization

Environmental Protection Agency, Technology Series report ~~number~~, EPA-660/2-73-030, December 1973. 168 p, 52 fig, 28 tab.

Pilot studies were conducted on two routes for recovery of volatile components in condensates from evaporation of spent liquors from acid sulfite pulping. The condensates were steam stripped prior to adsorption on activated carbon. The first route utilized fractional distillation and solvent extraction from the carbon, while the second route used low-temperature thermal regeneration. Relatively pure SO_2, methanol, furfural, and ethyl acetate were recovered. Estimated process economy, based upon recovery of saleable volatiles, favorable mass and heat balances, and credits for BOD removal, indicates the first route may provide a favorable method for the removal of pollutants from condensates. Low temperature regeneration studies failed due to mechanical design problems, but this second route continues to be considered as technically feasible. In an important auxiliary study, a substantial number of condensate samples from cooperating mills were analyzed. Differences in quality, quantity, and dilution of the condensates from different sources were apparent. Individual design of processing facilities for each mill is indicated, and especially so in those mills where backwashing of the evaporators contaminate the condensate with nonvolatile materials. (EPA)

*Waste water treatment, *Evaporators, *Condensation, Activated Carbon, Adsorption, Lignins, *Solvent Extraction, Separation Techniques, *Distillation, Alcohols, Acids, Organic Acids, ~~Sulfite~~ *Pulp Wastes, Pulp and Paper Industry, Biochemical Oxygen Demand, Chemical Oxygen Demand, Water Pollution, Industrial Wastes, Heat Balance, Mass Transfer, *Sulfite liquors

Steam Stripping, Fractional Distillation, Spent Sulfite Liquor, Acetic Acid, Methanol, Furfural, Ethyl Acetate, Volatile Acids, Neutral Volatiles, Nonvolatile Organics, Lignin, Lignosulfonic Acids.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

05D

~~Copy Available from GPO Sup Doc~~ as EP1.23: 660/2-73-030, $2.10; microfiche from NTIS as PB-233 139 $1.45

Security Class. (Report)

Security Class. (Page)

No. of Pages 181

Price 2.10-1.45

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U S DEPARTMENT OF THE INTERIOR
WASHINGTON, D C 20240

EPA-660/2-73-030
December 1973

TREATMENT OF SULFITE EVAPORATOR CONDENSATES FOR RECOVERY OF VOLATILE COMPONENTS

by

Kenneth W. Baierl
Nai L. Chang
Bernard F. Lueck
Averill J. Wiley
Robert A. Holm

Grant No. S801207
Program Element 1B2037

Project Officer

Ralph H. Scott
Chief, Paper and Forest Industries
U.S. Environmental Protection Agency
National Environmental Research Center
Corvallis, Oregon 97330

Prepared for

Office of Research and Development
U.S. Environmental Protection Agency
Washington, D.C. 20460

ia

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $2.10

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A pilot plant study of a process to recover the volatile constituents of the condensate derived from the evaporation of a sulfite spent wood pulping liquor has been made. The data from this one-year evaluation confirm prior work demonstrating that recovery of sulfur dioxide, furfural, methanol, and acetic acid (in the form of ethyl acetate) will yield reusable and salable materials, and provide either 60 or 90% BOD_5 reduction on the condensate depending on whether the condensate is contaminated by using it as wash liquor.

The work reported covers four major sections:

1. Assay of condensate samples from supporting mills,
2. Operation and data of a pilot system comprising steam stripping, activated carbon adsorption, and fractional distillation,
3. Mass, heat, and BOD_5 balances made according to the actual operating condition of the pilot plant at the Appleton Division mill of Consolidated Papers, Inc. to January 1973,
4. Low temperature (200°C-390°F) regeneration of carbon.

Assays of the condensate samples indicated a large variation in condensates from different mills which would necessitate tailoring of the complete process to the individual mill.

Operation of the pilot system, an extension of work previously done at the Scott Paper Company, has shown that the above-mentioned materials can be recovered as relatively pure products. Mass and heat balances, recoverable product values, and credits for BOD_5 removal combine to show the process to be a favorable avenue for the elimination of the pollution potential of the sulfite condensate waste.

The low temperature regeneration of carbon was an extension of work previously performed at The Institute of Paper Chemistry. This approach continues to be of interest and is considered to be technically feasible. However, all attempts to use the principles and equipment for electrical induction heating, as developed at the Lowell Technological Institute, failed due to mechanical design problems encountered in the pilot trials and which could not be developed and corrected within the time and funding available for this project.

This report was submitted in fulfillment of Grant No. S-801 207 under the partial sponsorship of the Environmental Protection Agency, by The Institute of Paper Chemistry with the Wisconson Department of Natural Resources and a group of pulp and paper mills cooperating. Work was completed as of May 1973.

CONTENTS

Sections		Page
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Assay of Condensate Samples From Supporting Mills	5
V	Design, Construction and Operation of Pilot System At The Appleton Mill of Consolidated Papers, Inc.	16
VI	Mass, Heat, and BOD_5 Balances	103
VII	Low Temperature Regeneration of Carbon	138
VIII	Invention Record and Publication	167

FIGURES

No.		Page
1	Scott Paper Company Pilot Plant Installation Everett Mill	18
2	IPC Pilot Plant — Consolidated Papers, Inc. Appleton Mill	20
3	Activated Carbon Column Furfural Regeneration	21
4	Activated Carbon Column Acetic Acid Regeneration	22
5	Methanol Removal *vs*. Stripping Steam Used — Scott Paper Company — 48-Inch (121.9 cm) Packing	28
6	Methanol Removal *vs*. Stripping Steam Used — Scott Paper Company — Variable Packing	29
7	Sulfur Dioxide Removal *vs*. Stripping Steam Used — Scott Paper Company — 48-Inch (121.9 cm) Packing	30
8	Sulfur Dioxide Removal *vs*. Stripping Steam Used — Scott Paper Company — Variable Packing	31
9	Methanol Removal *vs*. Stripping Steam Used — Consolidated Papers, Inc. — 48-Inch (212.9 cm) Packing	32
10	Methanol Removal *vs*. Stripping Steam Used — Consolidated Papers, Inc. — 12-Inch (30.48 cm) Packing	33
11	Sulfur Dioxide Removal *vs*. Stripping Steam Used — Consolidated Papers, Inc. — 48-Inch (121.9 cm) Packing	34
12	Sulfur Dioxide Removal *vs*. Stripping Steam Used — Consolidated Papers, Inc. — 12-Inch (30.48 cm) Packing	35
13	Acetic Acid Concentrations — Steam Stripping Column Feed and Bottoms	46
14	Acetic Acid Concentrations — Furfural Activated Carbon Column Feed and Effluent	47
15	Acetic Acid Concentrations — Acetic Acid Activated Carbon Column Feed and Effluent	48
16	Methanol Concentration — Steam Stripping Column Feed and Bottoms	49
17	Methanol Concentration — Furfural Activated Carbon Column Feed and Effluent	50
18	Methanol Concentration — Acetic Acid Activated Carbon Column Feed and Effluent	51
19	Biochemical Oxygen Demand — Steam Stripping and Activated Carbon Column Flows	52

Figures (Continued)

No.		Page
20	Organic Loosely Combined Sulfur Dioxide Concentrations — Steam Stripping and Activated Carbon Column Flows	53
21	Total Inorganic Sulfur Dioxide Concentrations — Steam Stripping and Activated Carbon Column Flows	54
22	pH — Steam Stripping and Activated Carbon Column Flows	55
23	Acetic Acid Concentrations — Steam Stripping and Activated Carbon Column Flows Using Regenerated Carbon	57
24	Methanol Concentrations — Steam Stripping and Activated Carbon Column Flows Using Regenerated Carbon	58
25	Total Inorganic Sulfur Dioxide Concentrations — Steam Stripping and Activated Carbon Column Flow Using Regenerated Carbon	59
26	Organic Loosely Combined Sulfur Dioxide Concentrations — Steam Stripping and Activated Carbon Column Flow Using Regenerated Carbon	60
27	Biochemical Oxygen Demand — Steam Stripping and Activated Carbon Column Flow Using Regenerated Carbon	61
28	pH — Steam Stripping and Activated Carbon Column Flow Using Regenerated Carbon	62
29	Furfural Concentrations — Steam Stripping and Furfural Activated Carbon Column Flows	64
30	Modified IPC Pilot Plant — Consolidated Papers, Inc. Appleton Mill	75
31	Both Activated Carbon Columns Regenerated with Ethanol	83
32	Steam Stripping, Furfural Activated Carbon and Acetic Acid Activated Carbon Columns	85
33	Steam Stripping, Furfural Activated Carbon and Acetic Acid Activated Carbon Columns	87
34	Process Flow	89
35	Regeneration — Step 1	90
36	Regeneration — Step 2	91
37	Regeneration — Step 3	92
38	Steam Stripping, Furfural Activated Carbon and Acetic Acid Activated Carbon Columns	95

Figures (Continued)

No.		Page
39	Suggested Regeneration	98
40	Projected Plant — Consolidated Papers, Inc. Appleton Mill	100
41	Suggested Commercial Application Consolidated Papers, Inc. Appleton Mill	101
42	Overall Mass Balances of the Pilot Plant	107
43	Separation Process — Mass Flow Sheet	108
44	Activated Carbon Regeneration and Furfural Recovery. 1. Furfural Recovery	109
45	Activated Carbon Regeneration and Furfural Recovery. 2. Methanol Recovery	110
46	Activated Carbon Regeneration and Ethyl Acetate Recovery. 1. Draining of Column	111
47	Activated Carbon Regeneration and Ethyl Acetate Recovery. 2. Recovery of Ethyl Acetate and Recovery of Ethanol	112
48	Separation Process	114
49	Activated Carbon Regeneration and Furfural Recovery	115
50	Activated Carbon Regeneration and Ethyl Acetate Recovery	116
51	Activated Carbon Thermal Regeneration Column	140
52	Location of Electrode and Thermocouple Terminals	142

TABLES

No.		Page
1	pH, Sulfur Dioxide, and Color Data	8
2	COD, BOD$_5$, and Acetic Acid and Formic Acid Data	9
3	Methanol, Acetic Acid, and Furfural Assays By Gas Chromatography and Calcium and Sodium Assays	10
4	Pollution Potential and Materials Data	14
5	Methanol Balance Steam Stripping Runs	38
6	Furfural Balance Steam Stripping Runs	41
7	Furfural Balance Activated Carbon Adsorption	65
8	Acetic Acid Balance Activated Carbon Adsorption	67
9	Evaporator Studies Data	76
10	Analyses of Evaporator Effects of Cooperator Mill	79
11	Carbon Adsorption Work at Scott Paper Company Oconto Falls Evaporator Condensate	79
12	Carbon Adsorption Work at Consolidated Papers, Inc. Appleton Div. Evaporator Condensate	79
13	Typical Activated Carbon Acetic Acid Column Regeneration Data — Potentially Patentable Process	94
14	Typical Pilot-Plant Operating Data	104
15	Typical Activated Carbon Acetic Acid Column Regeneration Data	105
16	Typical Activated Carbon Furfural Column Regeneration Data	106
17	Recoverable Values Based on the Condensate of Consolidated Papers, Inc.	135
18	Pollutional Balance Sheet	136
19	Lowell Unit — Direct Current	143
20	Lowell Unit — Direct Current	145
21	Lowell Unit — Direct Current	147
22	Lowell Unit — Direct Current	149
23	Lowell Unit — Direct Current	151
24	Lowell Unit — Alternating Current	154
25	Lowell Unit — Alternating Current	157
26	Lowell Unit — Alternating Current	160
27	Lowell Unit — Alternating Current	162
28	Lowell Unit — Alternating Current	164

ACKNOWLEDGMENTS

Sponsors of this project, in addition to Environmental Protection Agency and The Institute of Paper Chemistry, the prime contractor, were:

Organization	Authorized Representative
Wisconsin Department of Natural Resources	Everett D. Cann
American Can Company	Richard F. Benning
Consolidated Papers, Inc.	S. H. Dorcheus
Finch, Priyn & Company, Inc.	John Shema
Flambeau Paper Company	Walter A. Sherman
Great Northern Paper Company	V. F. Mattson
ITT Rayonier Inc.	J. J. Leithem
Masonite Corporation	H. A. Spalt
Publishers Paper Company	Zenon Rozycki
Scott Paper Company	Lyle J. Gordon
Wausau Paper Mills Company	Richard L. Post

The Project Director was A. J. Wiley, with direct supervision and engineering of the pilot plant operation under K. W. Baierl, assisted by John E. Baumann, pilot plant operator. The low-temperature carbon regeneration investigation was under the supervision of B. F. Lueck. Those responsible for and assisting in the laboratory phases were George A. Dubey, Arthur A. Webb, Gerald W. Hovind, Mrs. Linda Benkers, and Miss Gay Thurner. Engineering balance calculations were made by Nai L. Chang. With the exception of Mr. Chang, all are members of the IPC Effluent Processes Group, which is a section of the Division of Industrial and Environmental Systems headed by Robert A. Holm.

The support of the personnel of the Appleton Division of Consolidated Papers, Inc., especially W. R. Durdell, Plant Manager, and Dennis G. Wilch, who acted as liaison between the mill and IPC where the pilot plant was located, is acknowledged with sincere thanks.

SECTION I

CONCLUSIONS

Analyses of sulfite mill evaporator condensates submitted by sponsoring mills revealed that most of their condensates contained larger quantities of recoverable chemicals than were present in the relatively weak condensates available for processing at the Appleton Division mill of Consolidated Papers, Inc.

Data were compiled to assist interested sulfite pulp manufacturers toward making feasibility studies for utilizing steam stripping, fractionation, and activated carbon adsorption systems as tools toward solving their condensate pollution problems. With minimum additional pilot plant work tailored to individual mill requirements, these units can be reasonably scaled to commercial sizes with more accurate development of process economics. The newly developed activated carbon regeneration system appears economically feasible, but more optimization work could be worthwhile.

Low-temperature regeneration of activated carbon utilizing direct application of electric current through the carbon bed is not ready for commercial evaluation. The problems were identified, and can be used to evaluate further research potential.

SECTION II

RECOMMENDATIONS

Steam stripping, fractionation, and activated carbon adsorption have been demonstrated to be commercially feasible, and these unit processes are considered ready for a commercial demonstration plant. It is recommended that pilot work be continued on an individual mill basis, with the unit operations tailored toward establishing design data specific to each mill's ultimate objective. The data generated to date, including previous work at The Institute of Paper Chemistry, Scott Paper Company, and work under this project, should be used as the basis for future individual mill studies of plant design factors.

Future research work, supported collectively or individually, should follow the Process Options presented on page 73. These can be accomplished on laboratory or pilot plant bases. If time permits, a modular stepwise approach is recommended.

The established and developed analytical techniques can be used and/or extended in future studies.

The heat and material balances presented should be used as the bases for individual mill optimization work recommendations and future economic evaluations.

The newly developed activated carbon regeneration system should be optimized and fully evaluated with further pilot plant studies.

Finally, the same unit operations can be utilized to treat kraft evaporator condensates, which are also a potential source of stream and/or air pollution.

SECTION III

INTRODUCTION

Five years of research in two separate but complementary projects directed to removal of pollution-contributing materials from sulfite evaporator condensates have been conducted by The Institute of Paper Chemistry and by Scott Paper Company. The original studies have been advanced in this project by installation and operation of the pilot plant units in the Consolidated Papers, Inc.'s Appleton Division mill located in Appleton, Wisconsin. The systems developed at Scott Paper Company incorporated steam stripping, activated carbon adsorption and fractional distillation as means for removing and recovering sulfur dioxide, methanol, acetic acid, furfural, and other pollution-contributing materials, as well as regenerating the activated carbon.

The system previously studied at The Institute of Paper Chemistry consisted primarily in the removal of BOD_5 and COD contributing materials from these sulfite condensates by steam stripping and adsorption on activated carbon. Successful regeneration of the carbon was attained with low temperature heat (200°C-392°F) and the addition of superheated steam. Work under this project, herein described, consisted of the evaluation of a means of heating the carbon during regeneration by use of a system developed by Messrs. Bela M. Fabuss and Wilson C. Dubois of Lowell Technological Institute.

Mass, heat and BOD_5 balances are made according to the actual operating conditions of the pilot plant at the Appleton Division Mill of Consolidated Papers, Inc. and are based on data taken prior to January 17, 1973.

As an adjunct to this project, the sponsoring mills were invited to send samples of their evaporator condensate wastes to The Institute of Paper Chemistry for evaluation and comparison of their various constituents. Such a compilation of data would aid the personnel of the various mills to evaluate the process under study by comparison of their condensate to that of the Appleton Division of Consolidated Papers, Inc., where the pilot work was undertaken.

Data and discussion are presented in the following order:

1. Assay of condensate samples from supporting mills.
2. Design and construction of Pilot System at the Appleton mill of Consolidated Papers, Inc.
3. Mass, heat, and BOD_5 balances.
4. Low temperature (200°C-390°F) regeneration of carbon.

SECTION IV

ASSAY OF CONDENSATE SAMPLES FROM SUPPORTING MILLS

METHODOLOGY

Samples from ten mills of eight companies sponsoring this project, including samples from the Appleton Division of Consolidated Papers, Inc. taken during operation of the pilot-scale chemical recovery system, were received. The samples have been analyzed for 12 parameters. Most of the condensate samples showed greater potential for acetic acid and furfural recovery than is available in the condensate at the Consolidated mill. The content of a condensate varies with the pulping process and is substantially affected, first, by the type of wood cooked, second, by the nature of the cook and, third, by the pH of the liquor being concentrated.

METHODS OF ANALYSIS

The procedures used in these analyses are as follows:

pH

pH was determined on a Beckman pH meter.

Sulfur Dioxide

Two types of sulfur dioxide were determined; TI (total inorganic) and OLC (organic loosely combined). The total inorganic sulfur dioxide which is sometimes designated as free sulfur dioxide was determined by direct titration with standard iodine at 0°C (32°F). The organic loosely combined sulfur dioxide is that sulfur dioxide which is combined but which is readily releasted by treatment with alkali followed by acidification. It is determined by making the sample strongly alkaline with sodium hydroxide followed by acidification after one hour and titration with standard iodine at 0°C (32°C). This is the standard TAPPI procedure.

Color

A Hellige aqua tester was used to determine color. The sample is diluted as necessary and the color compared against standards which are equivalent to the cobalt platinum standards of "Standard Methods for the Examination of Water and Waste Water" of the American Public Health Association (APHA).

Chemical Oxygen Demand (COD)

The standard method of APHA was used, which consists of digestion of the sample with concentrated sulfuric acid and standard dichromate solution for two hours followed by back-titration with standard ferrous ammonium sulfate. Silver sulfate is used as a catalyst since without it the acetic acid would not be oxidized.

Biochemical Oxygen Demand (BOD_5)

The five-day BOD was determined by the dilution technique of standard methods of APHA. In all cases a series of dilutions were set up in duplicate and the dissolved oxygen determined with a Weston and Stack meter before and after the five-days incubation. Seeding was accomplished by using domestic sewage and BOD_5 was determined on a standard glucose-glutamic acid standard as a control for all procedures.

Volatile Organic Acids

The volatile organic acids generally present in spent sulfite liquors, and consequently in the condensate derived from these liquors, are acetic and formic. For many years the Effluent Processes Group has used an ether extraction procedure for determining these total volatile organic acids. The procedure consists of extraction with ether under acidic conditions using a ratio of 9 parts of ether to 1 part of sample, followed by titration with a standard alkali in the presence of a small amount of CO_2 free water. The volatile organic acids are then calculated in terms of equivalent acetic acid.

Formic Acid

The formic acid was determined from the residual remaining after the titration for the volatile organic acids. It was determined by removal of the ether by evaporation followed by acidification and reduction of mercuric chloride to mercurous chloride. The mercurous chloride is separated by filtration and determined by the addition of an excess of standard iodine followed by a back-titration with standard thiosulfate.

Acetic Acid

The acetic acid was determined by difference between total volatile organic acid and the formic acid.

Gas Chromatography

Methanol, furfural, and acetic acid were determined by gas chromatography using an Aerograph 1520 instrument. Separation was on a PORA PAC Q column. Butanol was used as an internal standard with a flame detector.

Calcium and Sodium

Both calcium and sodium were determined on a Beckman Flame Spectrophotometer reading at the appropriate wavelengths.

ASSAYS

Data covering the assays on the various samples received from the cooperators are given in Tables 1, 2, and 3. Origin of the samples is given only under a mill code letter. However, in order to compare with data being obtained in the operation of the process at the Consolidated mill, the composite data from that mill are identified as Sample No. 21, or Mill G. The data under Sample No. 21 are either averages of eight samples or assays performed on a composite of those eight samples. These samples were taken at periods during normal operation, which included channel switching of the Rosenblad evaporator.

Table 1. pH, SULFUR DIOXIDE, AND COLOR DATA

Mill	Sample number	Sample identification	pH	SO_2, mg/liter		Color[a]
				TI	OLC	
A	1	Dense hardwood 9/7/72	2.15	180	430	250
A	2	Dense hardwood 9/8/72	2.17	150	490	430
A	3	Dense hardwood 9/9/72	2.18	160	510	600
A	4	Aspen-dense hardwood 9/10/72	2.12	430	490	280
B	5	34% Hardwood, 66% softwood	1.78	787	919	60
B	6	Same as No. 5 but used for wash	3.02	6	108	400
B	7	93% Poplar, 7% spruce	2.44	28	270	90
B	8	Same as No. 7 but used for wash	3.21	8	600	100
B	18	14% Hardwood, 86% softwood	2.14	52	497	70
B	19	Same as No. 18 but used for wash	2.67	5	184	200
B	32	SSL, 34% Hardwood, 66% softwood	2.30	75	3398	20,000
B	33	34% Hardwood, 66% softwood	2.15	29	575	100
C	9	100% Aspen 9/19/72	2.63	102	264	500
C	10	100% Aspen 9/20/72	2.57	73	181	150
C	11	100% Aspen 9/22/72	2.50	236	474	750
C	12	100% Aspen 9/26/72	2.55	64	229	200
D	13	95% Aspen, 5% spruce combined condensate	2.63	13	110	15
D	14	95% Aspen, 5% spruce second effect	2.38	36	269	<5
D	24	95% Aspen, 5% spruce-combined condensate 1/24/73	2.43	102	161	<5
D	25	95% Aspen, 5% spruce second effect	2.18	270	357	<5
E	15	100% Hardwood	2.38	12	212	5
E	16	100% Softwood	2.27	596	427	5
E	17	Total discharge including surface condensate	2.32	54	1061	1000
F	20	Exploded wood pulp	3.54	0	0	650
F	22	Hardboard mill 12/20/72	3.25	2	16	300
F	23	Hardboard mill 1/4/73	3.30	1	4	300
G	21	Softwood	2.20	336	722	200
H	26[b]	Softwood, high solids effect	6.19	2.0	1.0	250
H	27[b]	Softwood, low solids effect	5.45	1.0	0.5	50
H	28	Softwood, 26 and 27 blend	5.69	1.3	0.2	150
H	29[c]	Softwood, total condensate	2.49	1.0	343	15
I	30	Magnefite softwood 2/2/73	2.79	76	74	<5
J	31	Magnefite softwood 2/5/73	2.37	380	107	10

---

[a] APHA Standard Color Units.

[b] From prestripped neutralized SSL.

[c] Total condensate from prestripped unneutralized SSL.

Table 2. COD, BOD_5, AND ACETIC AND FORMIC ACID DATA

Mill	Sample number	Sample identification	COD, mg/l	BOD_5, mg/l	Via ether extraction VOA[a], mg/l	Acetic acid, mg/l	Formic acid, mg/l
A	1	Dense hardwood 9/7/72	10140	6090	5998	5875	95
A	2	Dense hardwood 9/8/72	11016	6252	5876	5733	110
A	3	Dense hardwood 9/9/72	10822	6774	5415	5414	1
A	4	Aspen-dense hardwood 9/10/72	8769	5870	5326	5308	14
B	5	66% Hardwood, 34% softwood	12098	8884	6627	6550	59
B	6	Same as No. 5 but used for wash	9828	6480	5680	5570	84
B	7	93% Poplar, 7% spruce	12062	7890	6578	6523	42
B	8	Same as No. 7 but used for wash	10592	7416	7006	6964	32
B	18	14% Hardwood, 86% softwood	9487	7113	4282	4277	4
B	19	Same as No. 18 but used for wash	7743	6258	4532	4529	2
B	32	SSL, 34% hardwood, 66% softwood	173425	37425	5879	5550	252
B	33	34% Hardwood, 66% softwood	10400	6772	4633	4572	46
C	9	100% Aspen 9/19/72	11268	5586	4703	4650	41
C	10	100% Aspen 9/20/72	7859	5088	4978	4960	14
C	11	100% Aspen 9/22/72	16422	7456	5528	5471	44
C	12	100% Aspen 9/26/72	9780	6438	5894	5813	62
D	13	95% Aspen, 5% spruce combined condensate	5830	4476	2761	2618	110
D	14	95% Aspen, 5% spruce second effect	5830	4350	3023	2976	36
D	24	95% Aspen, 5% spruce combined condensate 1/24/73	5162	3870	2624	2591	25
D	25	95% Aspen, 5% spruce second effect 1/24/73	6330	4764	3584	3551	25
E	15	100% Hardwood	9272	7134	7280	7266	11
E	16	100% Softwood	6152	4506	4025	4022	2
E	17	Total discharge including surface condensate	30192	11100	5803	5800	2
F	20	Exploded wood pulp	3225	1730	1136	967	130
F	22	Hardboard mill 12/20/72	3445	1332	1624	1301	248
F	23	Hardboard mill 1/4/73	3393	2205	1567	1429	106
G	21	Softwood	7620	3718	2574	2514	47
H	26[b]	Softwood, high solids effect	900	118	61	40	17
H	27[b]	Softwood, low solids effect	2254	1566	38	17	16
H	28	Softwood, 26 and 27 blend	1694	1031	52	33	14
H	29[c]	Softwood, total condensate	3191	2334	1953	1896	43
I	30	Magnefite softwood 2/2/73	2981	1548	1325	1246	60
J	31	Magnefite softwood 2/5/73	3885	2358	2449	2350	60

---

[a] Volatile organic acids (VOA) in terms of acetic acid.
[b] From prestripped neutralized SSL.
[c] Total condensate from prestripped unneutralized SSL.

Table 3. METHANOL, ACETIC ACID, AND FURFURAL ASSAYS BY GAS CHROMATOGRAPHY AND CALCIUM AND SODIUM ASSAYS

			Via gas chromatography				
Mill	Sample number	Sample identification	MeOH, mg/l	Acetic acid, mg/l	Furfural, mg/l	Ca, mg/l	Na, mg/l
A	1	Dense hardwood 9/7/72	420	6260	630	90.9	2.0
A	2	Dense hardwood 9/8/72	530	5630	740	92.5	2.1
A	3	Dense hardwood 9/9/72	420	5000	740	119.5	2.2
A	4	Aspen-dense hardwood 9/10/72	370	4790	530	108.5	2.1
B	5	66% Hardwood, 34% softwood	1877	6057	2273	Trace	0.4
B	6	Same as No. 5 but used for wash	390	6200	575	24.6	0.6
B	7	93% Poplar, 7% spruce	915	7390	1485	Trace	0.5
B	8	Same as No. 7 but used for wash	405	7790	575	5.0	0.7
B	18	14% Hardwood, 86% softwood	1035	6100	1470	Trace	0.5
B	19	Same as No. 18 but used for wash	415	6045	535	55.0	0.7
B	32	SSL, 34% hardwood, 66% softwood	633	5533	1000	4.8	751
B	33	34% Hardwood, 66% softwood	850	6000	1800	Trace	Trace
C	9	100% Aspen 9/19/72	340	5372	283	298.5	1.4
C	10	100% Aspen 9/20/72	338	5472	365	123.0	0.7
C	11	100% Aspen 9/22/72	423	6088	362	498.5	3.0
C	12	100% Aspen 9/26/72	497	6473	447	191.0	1.2
D	13	95% Aspen, 5% spruce combined condensate	347	3837	323	Trace	0.6
D	14	95% Aspen, 5% spruce second effect	210	4217	235	Trace	0.4
D	24	95% Aspen, 5% spruce combined condensate 1/24/73	410	2730	300	Trace	1
D	25	95% Aspen, 5% spruce second effect 1/24/73	177	3770	133	None	Trace
E	15	100% Hardwood	130	7650	255	Trace	0.4
E	16	100% Softwood	520	5075	325	Trace	0.6
E	17	Total discharge including surface condensate	480	6930	517	894.0	2.2
F	20	Exploded wood pulp	127	1007	77	3.8	12.9
F	22	Hardboard mill 12/20/72	185	1450	285	1.5	5.9
F	23	Hardboard mill 1/4/73	200	1300	295	1.8	7.8
G	21	Softwood	620	2760	120	219.5	3.7
H	26[a]	Softwood, high solids effect	None	None	None	Trace	20.5
H	27[a]	Softwood, low solids effect	420	<300	None	Trace	2.1
H	28	Softwood, 26 and 27 blend	220	<300	None	Trace	9.8
H	29[b]	Softwood, total condensate	243	1943	190	Trace	1.3
I	30	Magnefite softwood 2/2/73	233	1533	160	Trace	0.5
J	31	Magnefite softwood 2/5/73	217	2100	107	Trace	0.8

---

[a] From prestripped neutralized SSL.
[b] Total condensate from prestripped unneutralized SSL.

Mill A cooks all hardwood and the samples submitted were daily composites taken by sampling at 15-minute intervals. It is not known if the samples from Mill B are grab samples or composites. However, there is a distinction between normal condensate and condensate used for wash. The samples from Mill C were from 100% hardwood and represent 8-hour composites covering a switching cycle on the Rosenblad evaporator. The samples from Mill D were from a mill cooking 95% aspen and 5% spruce by the magnesium bisulfite process. The combined condensate contained condensate from the second and third effects of a 3-effect evaporator, along with condensate from a surface condenser. The samples were 22-hour composites. Of the three samples submitted by Mill E, one is from a 100% hardwood cook, another from a 100% softwood cook and the third is a sample of the total condensate discharge. The samples from Mill F are condensates derived from a non-chemical cook. The four samples from Mill H were unique in that these condensates were derived from liquors that had received pretreatment prior to evaporation. Samples 26, 27, and 28 were derived from liquors that had been prestripped and neutralized, while Sample 29 was derived from a liquor that was prestripped only. All four samples were grab samples of 100% softwood origin. The samples from Mills I and J were derived from the evaporation of magnefite softwood liquors. Both were grab samples.

Table 1 contains pH, SO_2, and color data. The COD, BOD_5, and volatile organic acids, consisting of acetic and formic acid data, are given in Table 2. The data for the remainder of the assays, consisting of methanol, acetic acid, and furfural, as determined by gas chromatography, and assays for calcium and sodium are given in Table 3.

DISCUSSION

The pH of the various samples (Table 1) was between 2.12 and 3.30 for a spread of about 1.2, except in Sample 5 which had a pH of 1.78 and Samples 26, 27, and 28 which were preneutralized. There was a large variation in SO_2 content, both total inorganic and organic loosely combined, from the various mills, and even from samples derived from the same mill. This is the result of the cooking characteristics of each individual situation. From the viewpoint of the condensate chemical recovery process, those condensates containing relatively high SO_2 content will have to be steam stripped.

Most condensate samples upon aging will turn darker in color. So the color levels given in Table 1 are not necessarily indicative of what the fresh condensate would be. However, it is evident that some of this color is derived from lignin carry-over during evaporation or in some cases lignin entrainment when the condensate is used to wash the evaporator.

The BOD_5 (Table 2) is largely derived from the acetic acid, although in some cases the furfural and methanol are heavy contributors. As would be expected, the BOD_5 on condensates derived from hardwood liquors is considerably higher than those derived from softwoods. It is much easier to assess the source of the COD than for BOD_5. As an example, if one calculates the COD derived from the acetic acid, the formic acid, furfural, methanol, and SO_2 of Sample 21, a calculated COD of 4100 mg/l is obtained. Comparing this with a determined COD of 7620 mg/l shows that a good deal of the COD must be derived from liquor carry-over or from liquor entrained during washup of the evaporators. The high color content of 250 color units verifies this hypothesis. If one takes several other samples at random and determines the calculated COD on the same basis and compares it with the determined COD, the following results are obtained: Sample 1, calculated COD 8050 mg/l, determined COD 10,140 mg/l COD. Again the difference indicates relatively high lignin content and again this is verified by the high color content of 200 color units. Sample 18 had a calculated COD of 8,631 mg/l and a determined COD of 9,487 mg/l. Obviously, this sample contained much less liquor carry-over and this is verified by the lower color content of 70 color units. Sample 29 had a calculated COD of 2,811 mg/l and a determined COD of 3,191 mg/l, with a low color of 15 color units. Sample 31 had a calculated COD of 3,162 mg/l and a determined COD of

3,885 mg/l, with a color determination of 10 color units. It is quite obvious that these two latter samples contained a very small amount of liquor carry-over.

Assays performed by gas chromatography are given in Table 3. The methanol and furfural varied greatly in samples from various mills, as well as from samples from the same mill. The data from Mill D which submitted samples of condensate during normal operation and condensate that was used for washing, indicates a considerable loss in the methanol and furfural during the washing operation. Calcium levels varied considerably from mill to mill and from sample to sample within the mill. The two primary sources of calcium present in the condensate are from liquor carry-over and from removal of calcium from the evaporator in the washing cycle. The sodium content was so low that it appears to be of little or no consequence in these studies.

The data measuring the volatile pollution potential and materials found in these samples are given in Table 4 under categories of condensate derived from hardwoods and from softwoods. As would be expected, the acetic acid content of those samples derived from softwoods is generally lower than those derived from hardwood. There is no real trend in the methanol, formic acid, or SO_2 content of the condensates. The SO_2 content, of course, is mostly affected by the type and method of cooking the wood. The furfural content of the hardwoods is generally higher than those of the softwoods but there are exceptions. Since the furfural is derived from the pentoses present in the original liquor, it would be expected that the hardwoods would contain the higher furfural content, but the level of furfural present is greatly affected by the type of cook or method of evaporation utilized.

It will be noted that the acetic acid content was determined by two methods and that the gas chromatography method usually produced higher results than the ether extraction procedure. Extremely high acetic acid results by the gas chromatography method are attributable to interferences by unknown materials present in some of these condensates. No

Table 4. POLLUTION POTENTIAL AND MATERIALS DATA

Sample number	COD, mg/l	BOD$_5$, mg/l	Acetic acid, mg/l	MeOH, mg/l	Formic acid, mg/l	Furfural, mg/l	Total SO$_2$, mg/l
				Hardwood			
1	10140	6090	5875	420	95	630	610
2	11016	6252	5733	530	110	740	640
3	10822	6774	5414	420	1	740	670
4	8769	5870	5308	370	14	530	920
7[a]	12062	7890	6523	915	42	1485	298
8[a,e]	10592	7416	6964	405	32	575	608
9	11268	5586	4650	340	41	283	366
10	7859	5088	4960	338	14	365	254
11	16422	7456	5471	423	44	362	710
12	9780	6438	5813	497	62	447	293
13[d]	5830	4476	2618	347	110	323	123
14[d,f]	5830	4350	2976	210	36	235	305
15	9272	7134	7266	130	11	255	224
24[d]	5162	3870	2591	410	25	300	263
25[d,f]	6330	4764	3551	177	25	133	627
				Softwood			
16	6152	4506	4022	520	2	325	1023
18[b]	9487	7113	4277	1035	4	1470	549
19[b,e]	7743	6258	4529	415	2	535	189
21	7620	3718	2514	620	47	120	1058
29[c]	3191	2334	1896	243	43	190	344
30	2981	1548	1246	233	60	160	150
31	3885	2358	2350	217	60	107	487

---

[a] 93% Hardwood, 7% softwood.
[b] 86% Softwood, 14% hardwood.
[c] From prestripped SSL.
[d] 95% Aspen, 5% spruce.
[e] Used for wash.
[f] Second effect.

effort was made to alter the gas chromatography procedure to alleviate this problem, since the ether extraction procedure had also been used.

CONCLUSIONS

The analysis of the condensate samples submitted by sponsors of this project have indicated the potential amount of SO_2, acetic acid, methanol, and furfural that would be available for recovery. For most of the participating mills, the output of these components would exceed the recoverable chemicals available in the condensate from the Consolidated mill where the system was under pilot-scale study.

SECTION V

DESIGN, CONSTRUCTION AND OPERATION OF PILOT SYSTEM AT THE APPLETON MILL OF CONSOLIDATED PAPERS, INC.

PREVIOUS WORK

Initial work in Scott Paper Company's Everett Mill was done using 4 inch D x 4 ft H glass pipe for all operations. Four activated carbon columns were placed in series to study the selective adsorption of methanol, furfural, and acetic acid in aqueous solutions by granular activated carbon. Filtrasorb 400 was used. This work showed that:

1. Methanol came out of Column 1 in 15 minutes, Column 2 in 30 minutes, Column 3 in 45 minutes, and Column 4 in an hour.
2. Acetic acid came out of Column 1 in 1 hour, Column 2 in 2-1/2 hours, Column 3 in 3 hours 50 minutes, and Column 4 in 4 hours 50 minutes. Furfural did not come out of Column 1 after more than 10 hours of operation.

At the start all columns had the activated carbon flooded with water. It takes approximately 10 minutes for the water to be displaced with feed in each column (40 minutes for total displacement assuming plug flow), so only the break through, not full loading, was used for calculating the following carbon loadings.

Methanol Loading — Four Columns

$$\begin{aligned} CH_3OH &= 12.6 \text{ gph } (1 \text{ hour}) (8.33 \text{ lb/gal.}) (0.00049) \\ &= 0.0514 \text{ lb} \quad 23.3 \text{ g} \end{aligned}$$

$$\begin{aligned} CH_3OH \text{ Loading} &= 0.0514 \text{ lb}/28.4 \text{ lb carbon} \\ &= 0.00181 \text{ lb/lb carbon} \\ &= 0.00181 \text{ g/g carbon} \end{aligned}$$

Acetic Acid Loading — Four Columns

$$\begin{aligned} CH_3COOH &= 12.6 \text{ gph } (5 \text{ hours}) (8.33 \text{ lb/gal.}) (0.0053) \\ &= 2.78 \text{ lb} \quad 1.26 \text{ kg} \end{aligned}$$

CH_3COOH Loading = 2.78 lb/28.4 lb carbon
= 0.098 lb/lb carbon
= 0.098 g/g carbon

Furfural Loading — First Column

C_4H_3OCHO = 12.6 gph (10.1 hours) (8.33 lb/gal) (0.00048)
= 0.508 lb 0.23 kg

C_4H_3OCHO Loading = 0.508/7.08 = 0.0718 lb/lb carbon
= 0.0718 g/g carbon

Therefore, it was necessary to remove methanol by steam stripping and/or fractionation. Using various combinations of steam stripping and fractionation column operations, the following products were recovered:

85% + by weight SO_2 vapor

90% + by weight methanol

90% + by weight furfural

These results provided two possibilities for furfural removal and potential recovery, fractionation and/or adsorption by activated carbon.

Using these data, a pilot plant was built at Scott's Everett Mill using new, existing and scrap equipment to study recovery of volatile chemicals from the Everett mill hot water accumulator overflow (blow gas condensates). Essentially, it consisted of 4 inch (10.2 cm D) diameter glass piping with steel plates and reflux splitters, and two 10 inch (25.4 cm) diameter stainless steel adsorbers (also used as reactors during regeneration) complete with column packings, heat exchangers, and pumps. This equipment presented the opportunity to inexpensively experiment with various combinations of steam stripping, fractionating and/or adsorbing operations. Scott Paper Company used this pilot plant equipment in their Everett, Washington mill to study chemical recovery from clean evaporator and blow gas condensates. The equipment had been installed and operated as shown on Fig. 1. All the above mentioned chemicals, as well as 90%+ by weight ethyl acetate, were recovered. Patents covering the processes, as well as their

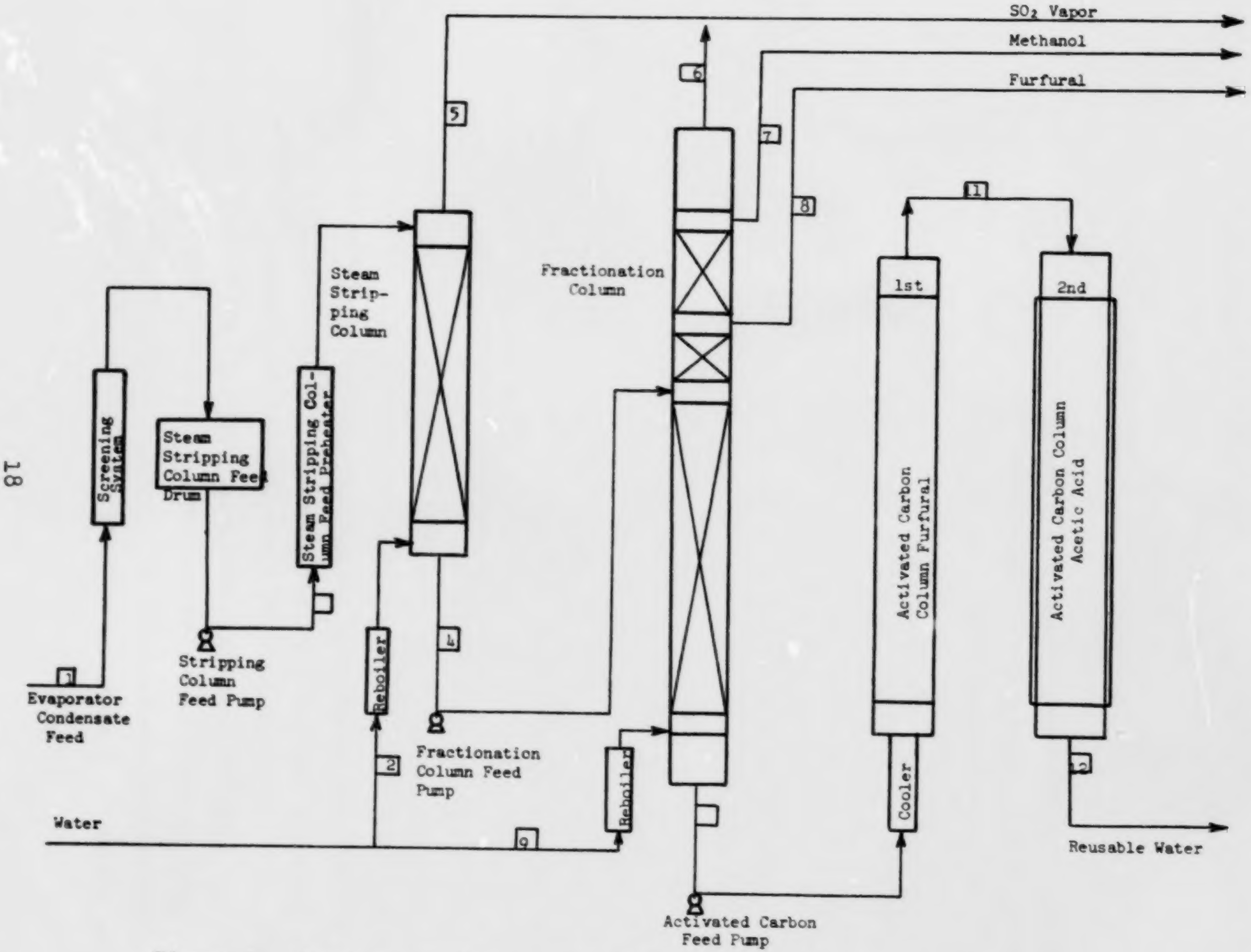

SO₂ Vapor
Methanol
Furfural
6
5
7
8
11
Fractionation Column
Steam Stripping Column
1st
2nd
Screening System
Steam Stripping Column Feed Drum
Steam Stripping Column Feed Preheater
Activated Carbon Column Furfural
Activated Carbon Column Acetic Acid
1
Evaporator Condensate Feed
Stripping Column Feed Pump
Reboiler
4
2
Fractionation Column Feed Pump
Water
9
Reboiler
Cooler
12
Reusable Water
Activated Carbon Feed Pump

Figure 1. Scott Paper Company pilot plant installation Everett mill

adaptability to kraft condensates, were applied for by the Scott Paper Company in 1971.

METHODOLOGY

In July, 1972 the pilot plant at Everett was dismantled and shipped to Appleton. Since preliminary analyses of Consolidated's evaporator condensates showed their methanol, acetic acid, and furfural compositions considerably lower than those encountered at Scott, the initial pilot plant units were arranged as shown on Fig. 2. The activated carbon regeneration systems were built as shown on Fig. 3 and 4. No more than 50 minutes storage capacity was provided for storing the evaporator condensate fed to the pilot plant area. No special arrangements were made with Consolidated Papers, Inc.'s operating personnel. The evaporator condensate was sent to the pilot plant in the same manner that it was drained. The main differences between this work and that done previously were:

1. The evaporator condensate was processed within minutes after it was produced in the evaporators. Previous work was done on condensates that had set long period of time (weeks) before they were processed.
2. At times, portions were received of this condensate which had been used to wash scale, fibers and spent sulfite liquor from the evaporator surfaces. Previously only clean condensate was used.

One purpose of this pilot plant project was to prove the processes developed could handle evaporator condensate after it had been used to wash the evaporator surfaces. It was also desired to provide a choice of commercially feasible alternatives for processing of evaporator condensates, with recovery of saleable values wherever possible to help pay the costs of disposal processing of this waste flow from acid sulfite mills equipped with evaporators. It was anticipated that more than one possible route to recovery of these volatile components would

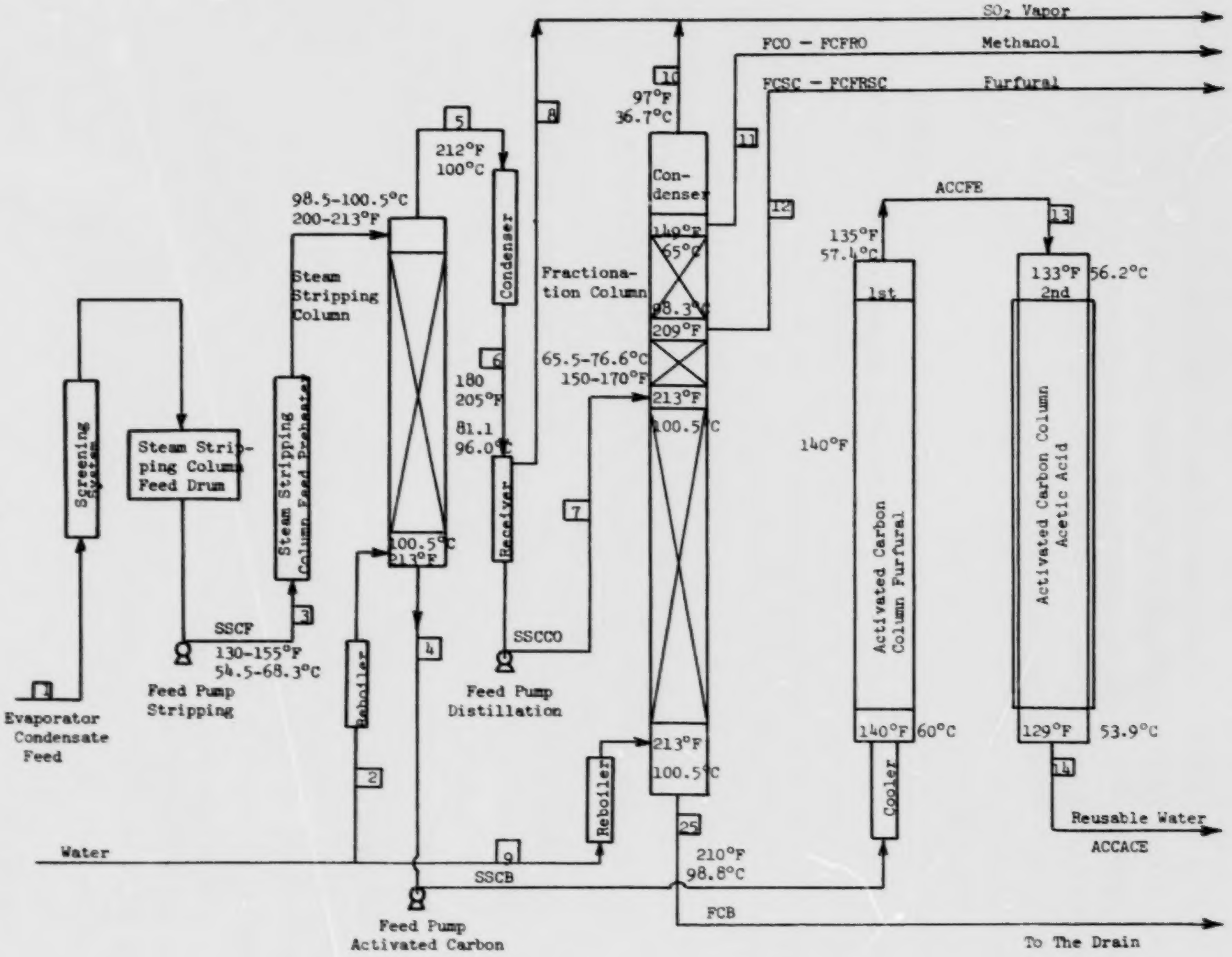

SO₂ Vapor
Methanol
Furfural
FCO — FCFRO
FCSC — FCFRSC
10
97°F
36.7°C
11
12
8
5
212°F
100°C
98.5-100.5°C
200-213°F
Steam Stripping Column
Condenser
Con-denser
Fractiona-tion Column
140°F
65°C
98.3°C
209°F
213°F
100.5°C
65.5-76.6°C
150-170°F
6
180
205°F
81.1
96.0°C
Screening System
Steam Stripping Column Feed Drum
Steam Stripping Column Feed Preheater
100.5°C
213°F
Receiver
7
3
SSCF
130-155°F
54.5-68.3°C
4
SSCCO
1
Evaporator Condensate Feed
Feed Pump Stripping
Reboiler
Feed Pump Distillation
2
Water
9
SSCB
Reboiler
213°F
100.5°C
25
210°F
98.8°C
Feed Pump Activated Carbon
FCB
To The Drain
ACCFE
13
135°F
57.4°C
1st
133°F
56.2°C
2nd
140°F
Activated Carbon Column Furfural
Activated Carbon Column Acetic Acid
140°F
60°C
129°F
53.9°C
Cooler
14
Reusable Water
ACCACE

Figure 2. IPC pilot plant — Consolidated Papers, Inc. Appleton Mill

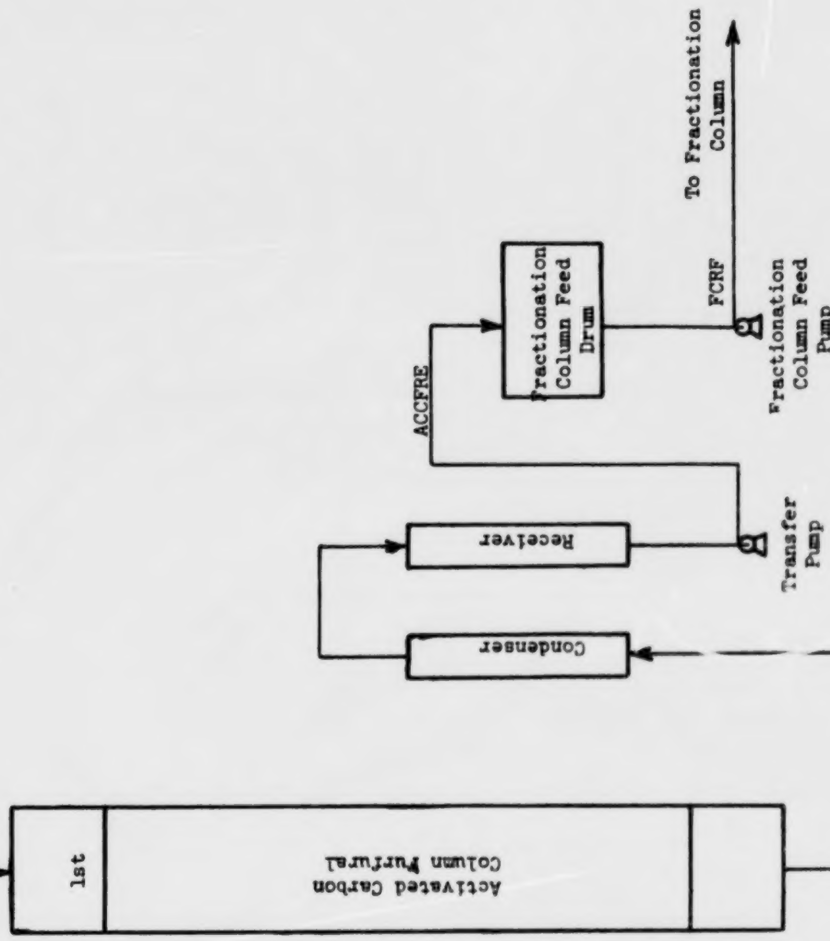

Methanol from Fractionation Column
Water
Methanol Feed Drum
Methanol Feed Pump
ACCFRI
Heat Exchange Methanol Vaporizer
1st
Activated Carbon Column Furfural
Condenser
Receiver
Transfer Pump
ACCFRE
Fractionation Column Feed Drum
FCRF
Fractionation Column Feed Pump
To Fractionation Column

Figure 3. Activated carbon column furfural regeneration

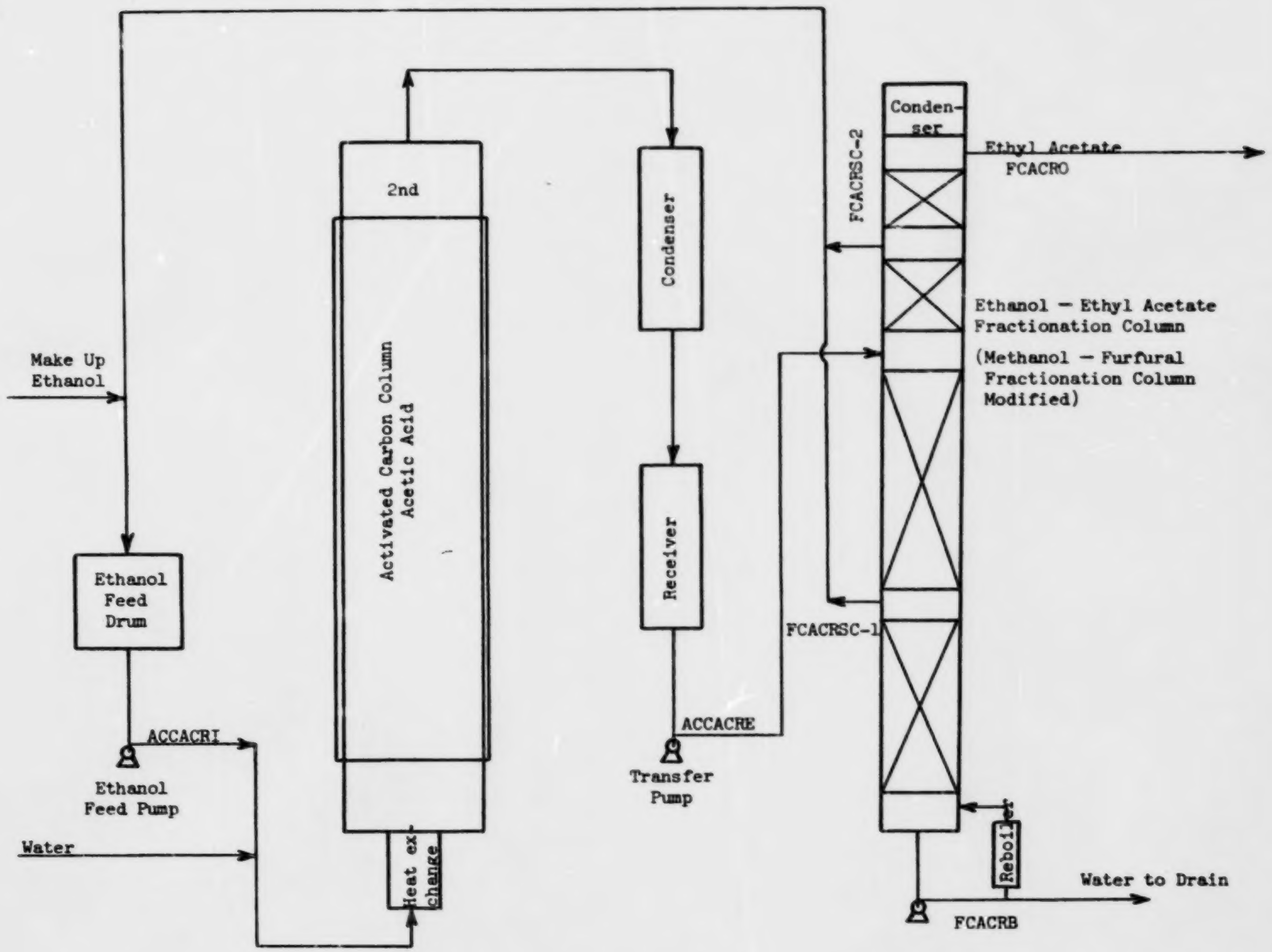

Make Up
Ethanol
Ethanol
Feed
Drum
ACCACRI
Ethanol
Feed Pump
Water
Heat ex-
change
2nd
Activated Carbon Column
Acetic Acid
Condenser
Receiver
ACCACRE
Transfer
Pump
FCACRSC-2
FCACRSC-1
Conden-
ser
Ethyl Acetate
FCACRO
Ethanol — Ethyl Acetate
Fractionation Column
(Methanol — Furfural
Fractionation Column
Modified)
Reboiler
Water to Drain
FCACRB

Figure 4. Activated carbon column acetic acid regeneration

be developed in ways which would fit the variety of operating conditions in the various sulfite pulp mills supporting this project.

The initial pilot plant constructed as per Fig. 2 was not a replica of the one at Scott's Everett Mill. The flow pattern was more advanced and tailored to the needs of the Appleton Div. of Consolidated Papers, Inc. For simplification it will be discussed in five parts: the feed system, steam stripping column system, fractionation column system, the activated carbon adsorption system, and the activated carbon regeneration system.

Feed

The evaporator condensate was pumped by means of a transfer pump from the evaporator area through the pilot plant area to the river through a 2-inch diameter stainless steel pipe. The feed was tapped off this transfer line and run through a screening system to remove particulate material (fibers and evaporator scale) to protect the stainless steel mesh packing in the stripping column. From the screening system it went into a 55-gallon (208-liter) stainless steel feed drum. From this drum it was pumped by two small Eastern pumps in series through the feed preheater to the steam stripping column. Two pumps were required, because one pump could not constantly deliver the required flow when back pressures exceeded 15 psig (1.05 kg/cm^3 gage). No effort was made to determine the scale and fiber content as the amounts varied. It was established, however, that scale and fiber were in the evaporator condensate and had to be removed. Excellent screening performance was attested to, since the steam stripping column did not require cleaning for a period extending back over three years of operation in Appleton and Everett.

Steam Stripping

The steam stripping system consisted of the preheater, steam stripping column, reboiler, condenser, and receiver. The preheater was used to bring the evaporator condensate up to its boiling point, 209 to 211°F

(98.3 to 99.4°C). The stripping column is 4 inch (10.2 cm) diameter and contains a 4 ft (121.9 cm) height of packing. The packing used was Goodloe 316 S.S. mesh. The evaporator condensate was fed into the top of the column and steam was fed into the bottom. The steam rate was controlled by pumping water into the reboiler and super-heating it indirectly with steam. In that way all the water was converted to steam. The vapor left the top and flowed down through the condenser. The condensed vapor was collected in the 4 inch (10.2 cm) diameter glass receiver. By controlling the temperature of the vapor leaving the receiver at 205 (96.1) to 190°F (87.8°C), the SO_2 concentration in the exhaust vapor was controlled. The steam stripped evaporator condensate was pumped from the bottom of the column to the first activated carbon column. The feed rate capability was 1.5 gpm maximum (5.7 liters per minute). Plans were made to evaluate the steam stripping column system while varying the feed rates from 0.5 to 1.5 gpm (1.9 to 5.7 liters per minute) and using 2 to 12% by weight of feed stripping steam.

Fractionation

The fractionation system consisted of a fractionation column, a reboiler and a condenser. The fractionation column had four packed sections of 4 inch (10.2 cm) diameter x 4 ft (121.9 cm) high glass piping between the feed and bottom of the column [16 ft (487.7 cm) of packing total], one packed section of 4 inch (10.2 cm) diameter x 4 inch (121.9 cm) high glass piping between the feed and the first reflux splitter [4 ft (121.9 cm) of packing] and one packed section of 4 inch (10.2 cm) diameter x 2 ft (61.0 cm) high glass piping between the first splitter and top splitter [2 ft (61.0 cm) of packing]. All packing were Goodloe S.S. mesh. The condenser was directly above the top reflux splitter. The reboiler was operated the same as that on the steam stripping column to ensure complete vaporization.

Initially, condensed overheads from the steam stripping columns were fed into this system. Sulfur dioxide as a vapor was vented through the top of the condenser, a methanol crude was withdrawn from the top splitter and a furfural crude from the bottom splitter. Disposal of the bottoms from the fractionation column was to be studied. In a commercial operation they might be sent back to the evaporators, since the material they contain were no longer volatile. However, this could involve about a 10% increase in evaporation load. This raised the question of how many participating mills could handle a 10% increase in evaporation load. Plans were to operate this column in conjunction with the feed and steam stripping column systems, and study the effect of the steam stripping operation on this column and its product purities.

Activated Carbon Adsorption

The activated carbon adsorption system consisted of a feed pump, heat exchanger to control the temperature of the steam stripped evaporator condensate to the carbon columns, and 10 inch I.D. (25.4 cm) stainless steel columns. The first one was fed up-flow and the second one, which was jacketed, down-flow. The liquid level in the second column was controlled above the carbon by running the discharge tubing higher than the top of the column. Disengaging sections were provided over and under the columns. Temperature and pressure measurements were taken in these sections in both columns. In the nonjacketed column there was a connection for temperature and pressure readings in the middle. The discharge condensate was piped to the drain. The nonjacketed column contained 98 pounds (44.5 kg) of Filtrasorb 400 granular carbon and the jacketed one 110 pounds (49.9 kg). The purpose was to study the benefits of selective adsorption of acetic acid, furfural, and polymerized material in the two carbon columns, and to evaluate the effectiveness of the developed carbon regeneration systems.

Activated Carbon Regeneration

The initial activated carbon regeneration systems were built as shown on Fig. 3 and 4. These systems were identical to those developed and used in Scott Paper Company's Everett Mill's pilot plant. For recovery of furfural, polymerized material and that adsorbed portion of spent sulfite liquor, methanol was pumped from the feed drum through a heat exchanger where it was vaporized and slightly superheated. The superheated vapor entered the top of the carbon column and forced the condensed methanol, water, furfural, polymerized material and that adsorbed portion of spent sulfite liquor out the bottom. The first portion of liquid removed, approximately 10 gallons (37.8 liters) was drained. Analyses had shown it to contain less furfural and roughly the same amount of methanol and acetic acid as in the feed to the column. Eventually, higher concentrations of methanol, furfural, and residual material came through as a liquid. Finally, the methanol vapor came out the bottom, and was condensed and collected in the receiver. Once the condensed methanol vapor contained only trace quantities of furfural, water was fed into the vaporizer to produce steam. The steam forced the methanol vapor out of the carbon. The methanol was condensed, collected in the receiver, and pumped into the fractionation column for eventual recovery. When only steam remained in the column, the steam stripped evaporator condensate, cooled, was pumped into the carbon column displacing and condensing the steam. The carbon column was thus back on its normal adsorption cycle. The methanol and furfural were recovered in the fractionation column in the same manner as described for recovering them from the steam stripping column condensed overhead vapors. The polymerized material and residual spent sulfite liquor were held in the bottom of the fractionation column. When the concentration (over 20% by weight) affected the pumps recirculation rate or when there was an excessive amount of water, it was discharged to the drain.

Activated carbon serves as a catalyst for the esterification of acetic acid with ethanol in the vapor phase and the resultant ethyl acetate is a readily marketable product. These facts provided the bases for choosing ethanol as the regenerating agent for the second activated carbon column. Figure 4 shows the manner in which the vaporized ethanol was passed upward through it. This column was jacketed for steam to prevent condensation in the carbon. The overhead vapors were then condensed and collected in a receiver. From the receiver the condensate was fed into a fractionation column. Ethyl acetate was collected overhead, and ethanol was recycled from a point about one third of the height from the bottom of the column back through the carbon column. Water recycled back through the activated carbon system and was removed from the bottom of the column. The reboiler was used to control the top reflux and the vaporization of ethyl acetate.

EXPERIMENTAL OPERATION AND EVALUATION OF PILOT PLANT

Steam Stripping

At the September, 1972 meeting of the project sponsors, plans to evaluate the steam stripping column system varying feed rates from 0.5 to 1.5 gpm (1.9 to 5.7 liters per minute) and using 2 to 12% by weight of feed stripping steam were reported. The height of the column packing was to be varied under similar operating conditions. This work was completed with the equipment set up as shown in Fig. 2. The trouble points when operating this system were:

1. Controlling the temperature of the evaporator condensate feed entering the column at its bubble point.
2. Maintaining a constant pressure drop across the column packing.
3. Controlling the condenser so as to maintain a constant temperature for the condensed steam stripping column overhead vapors.
4. Maintaining a constant back pressure from the SO_2 venting system.

All of these were related to the concentration of the volatile chemicals in the evaporator condensate feed.

To compare Consolidated Papers, Inc.'s Appleton Div. Mill evaporator condensate steam stripping data with that of Scott Paper Company's Everett Mill blow gas condensate steam stripping data, refer to Fig. 5 to 12. For a fair comparison keep these points in mind. At Everett

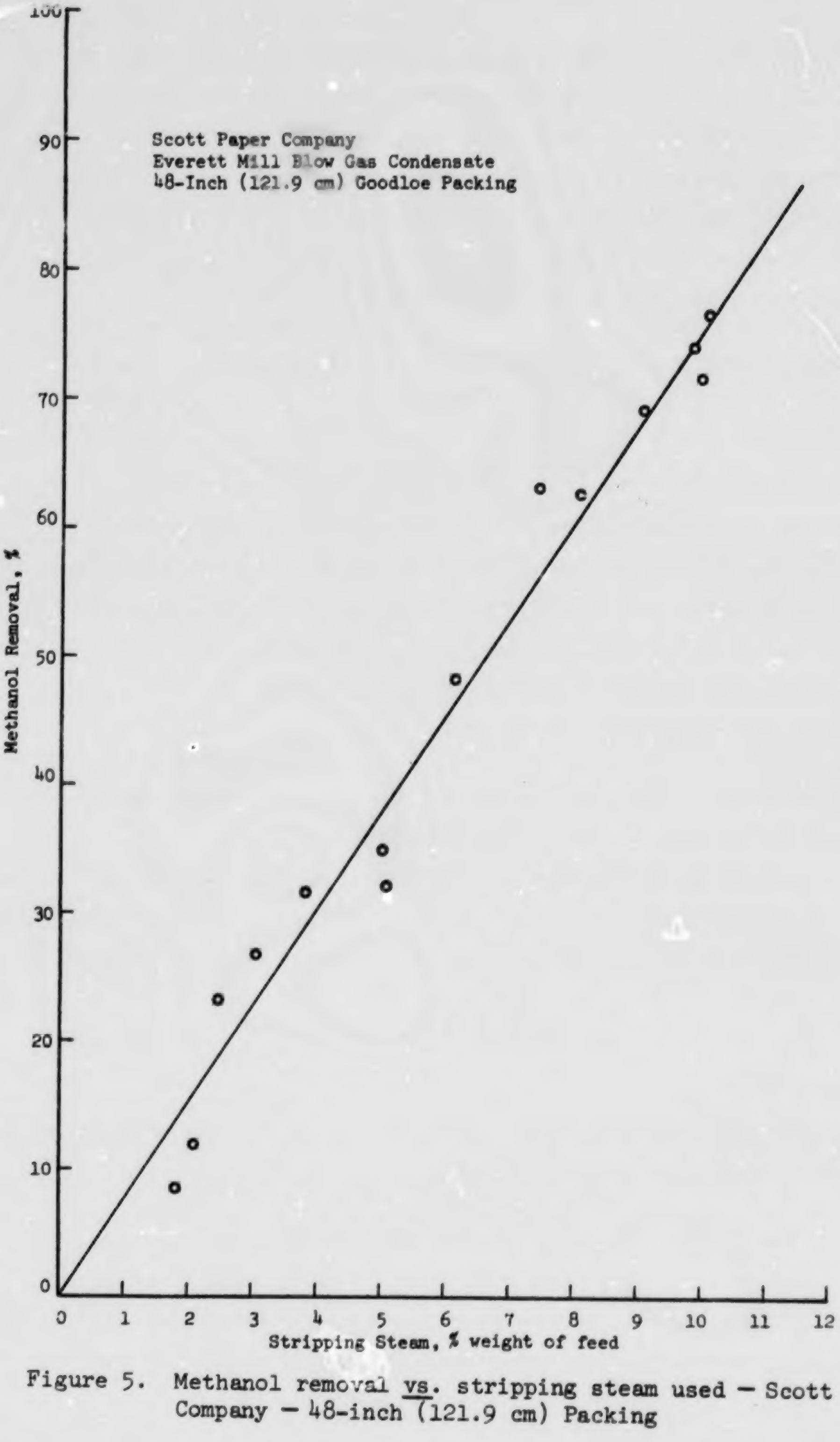


Figure 5. Methanol removal *vs.* stripping steam used — Scott Paper Company — 48-inch (121.9 cm) Packing

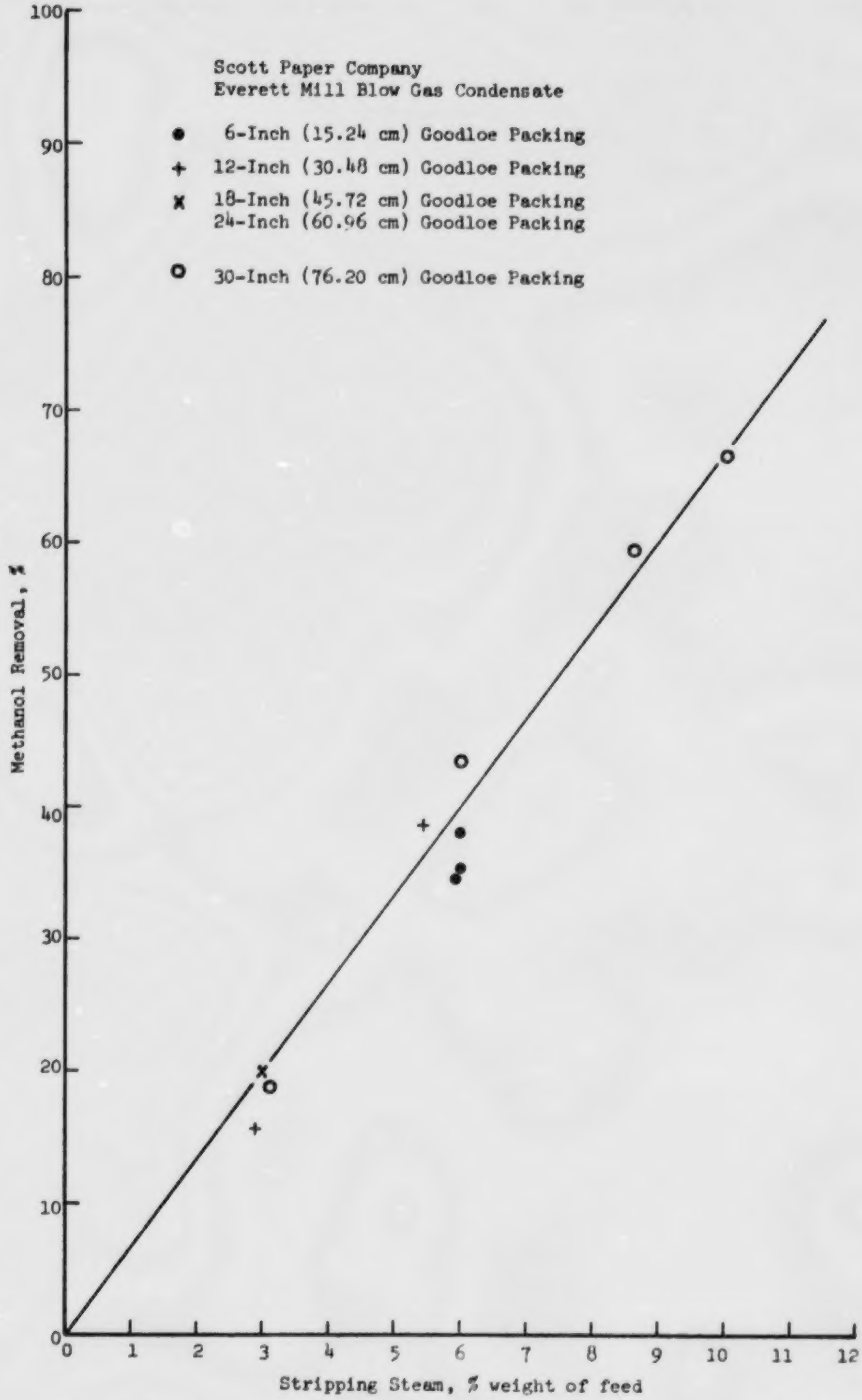


Figure 6. Methanol removal vs. stripping steam used — Scott Paper Company — variable packing

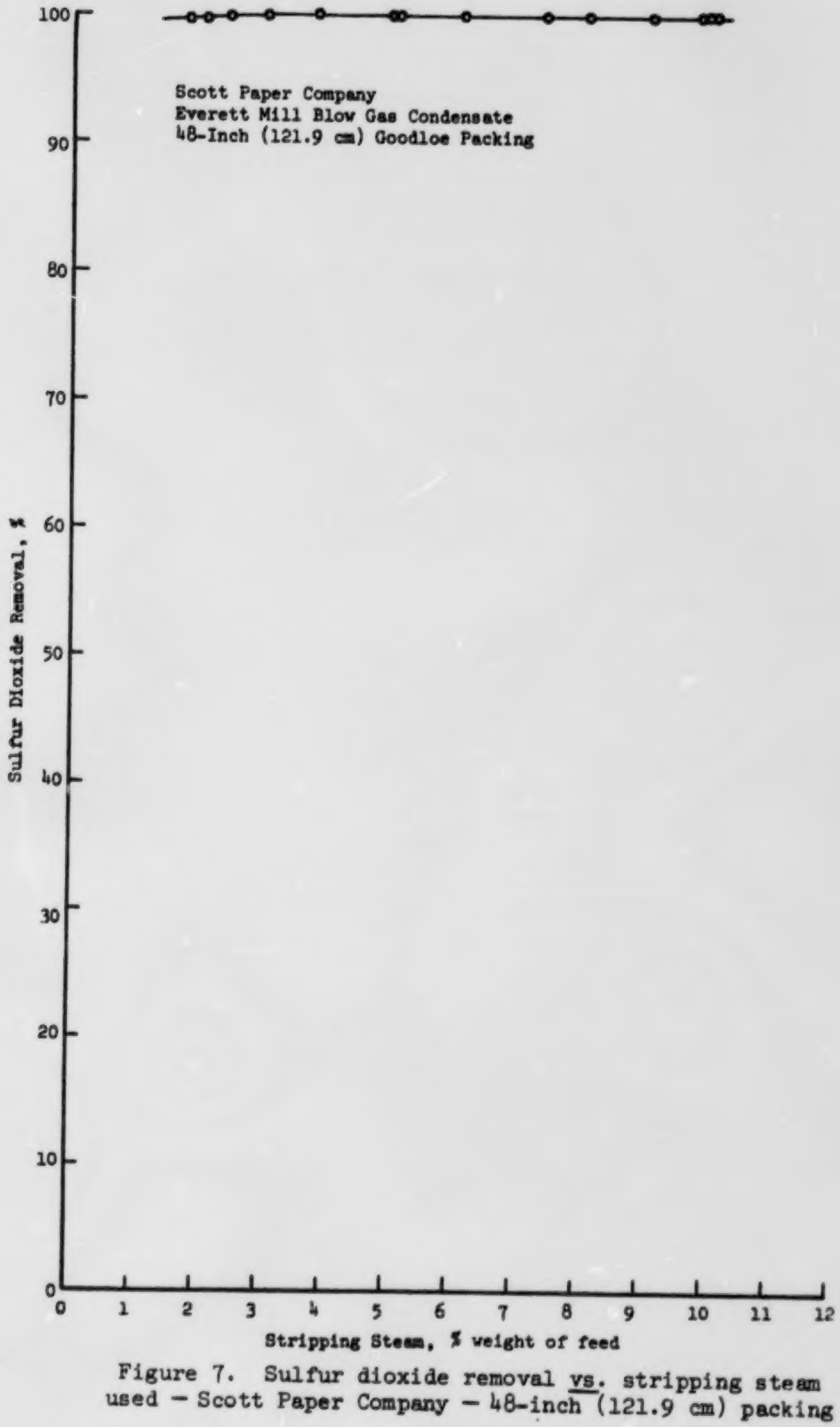


Figure 7. Sulfur dioxide removal vs. stripping steam used — Scott Paper Company — 48-inch (121.9 cm) packing

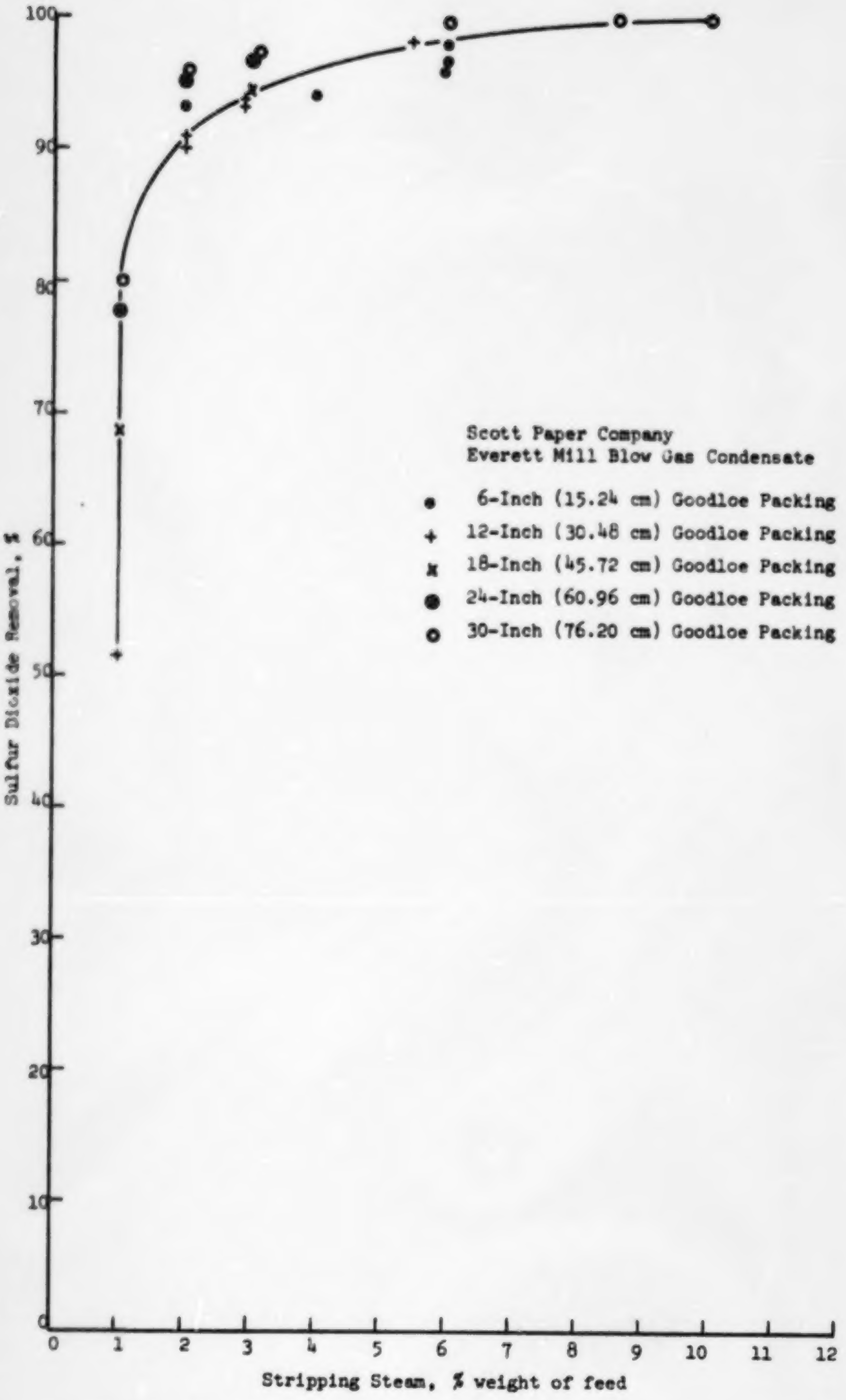


Figure 8. Sulfur dioxide removal *vs*. stripping steam used — Scott Paper Company — variable packing

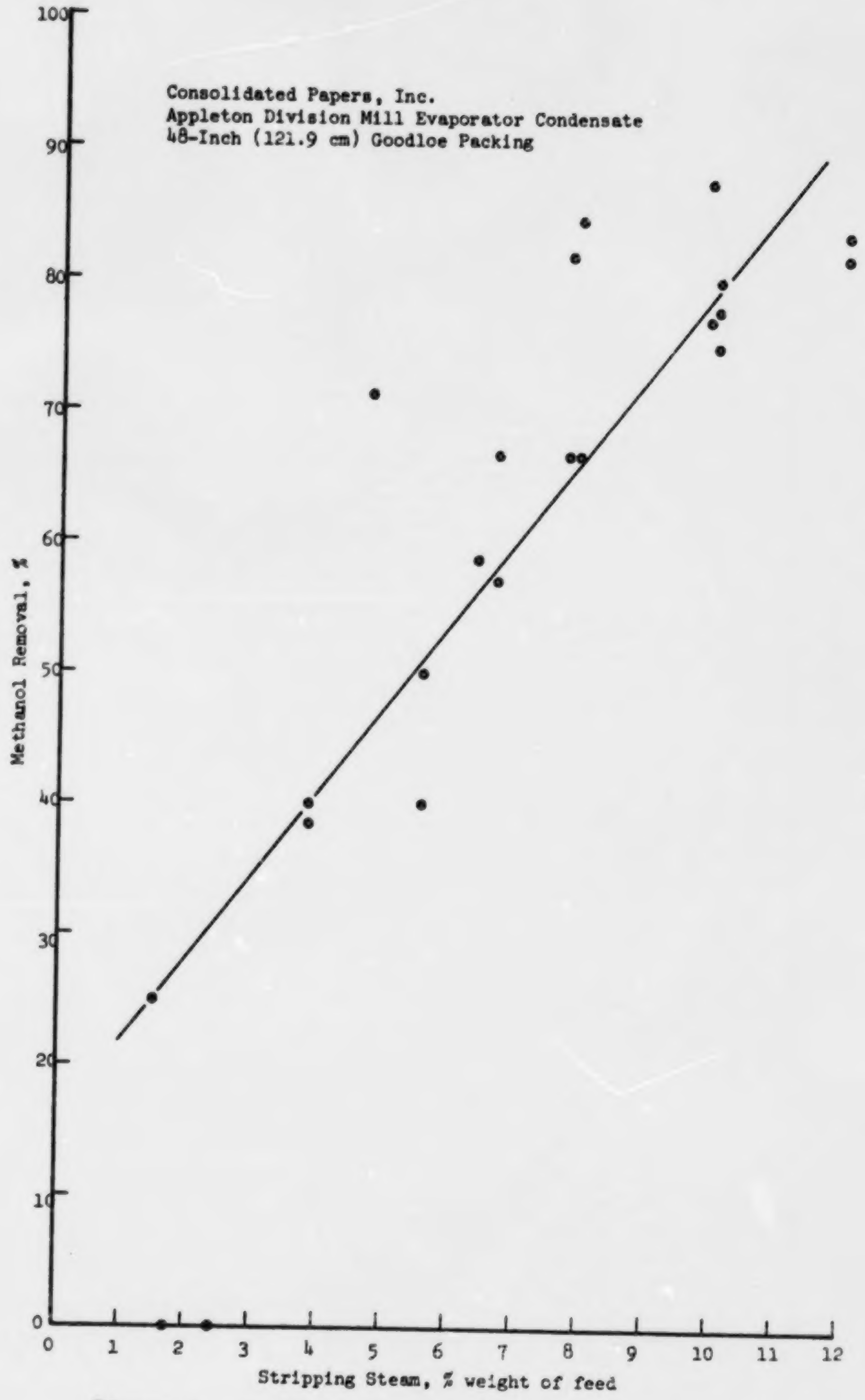


Figure 9. Methanol removal vs. stripping steam used — Consolidated Papers, Inc. — 48-inch (212.9 cm) packing

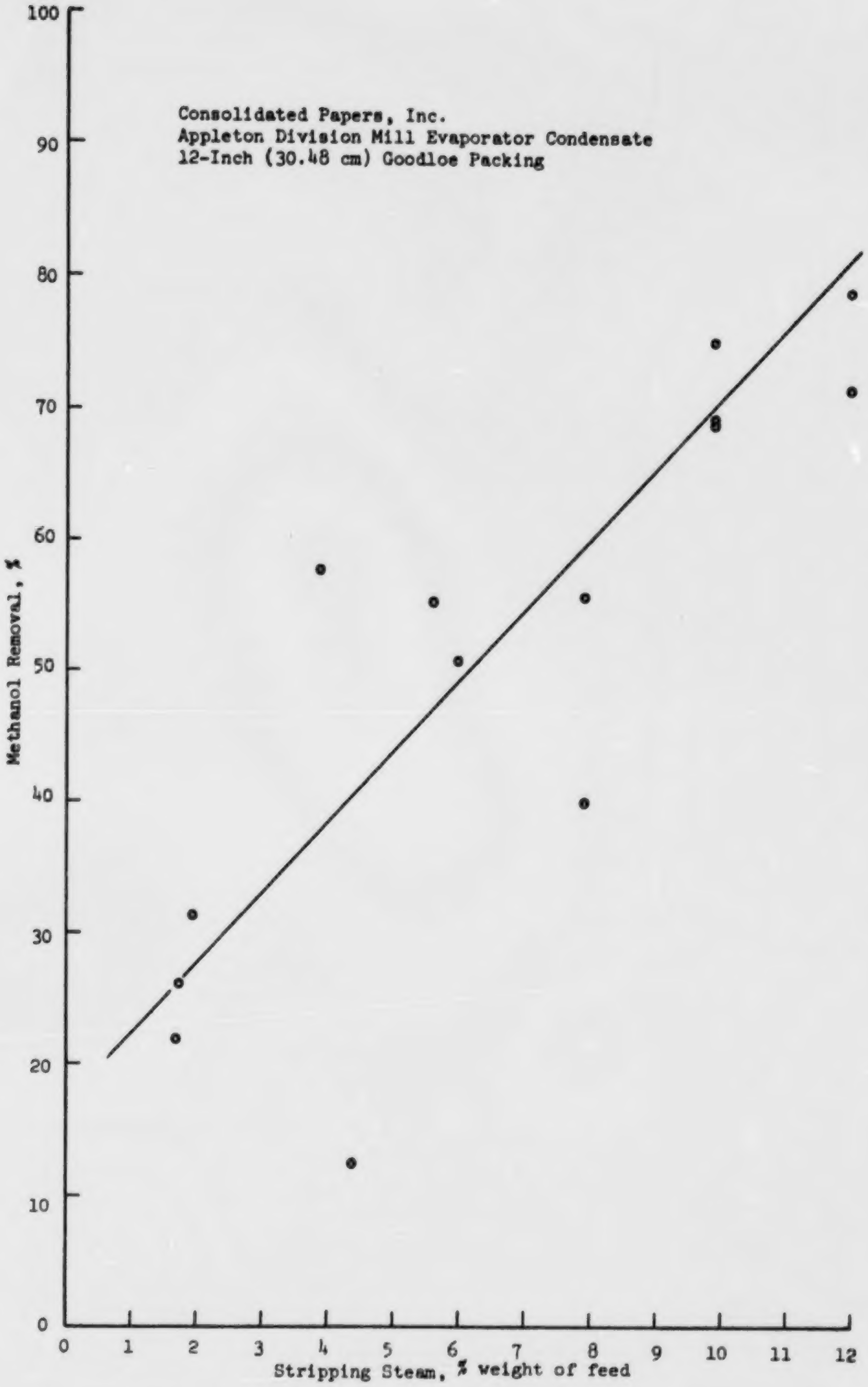


Figure 10. Methanol removal vs. stripping steam used — Consolidated Papers, Inc. — 12-inch (30.48 cm) packing

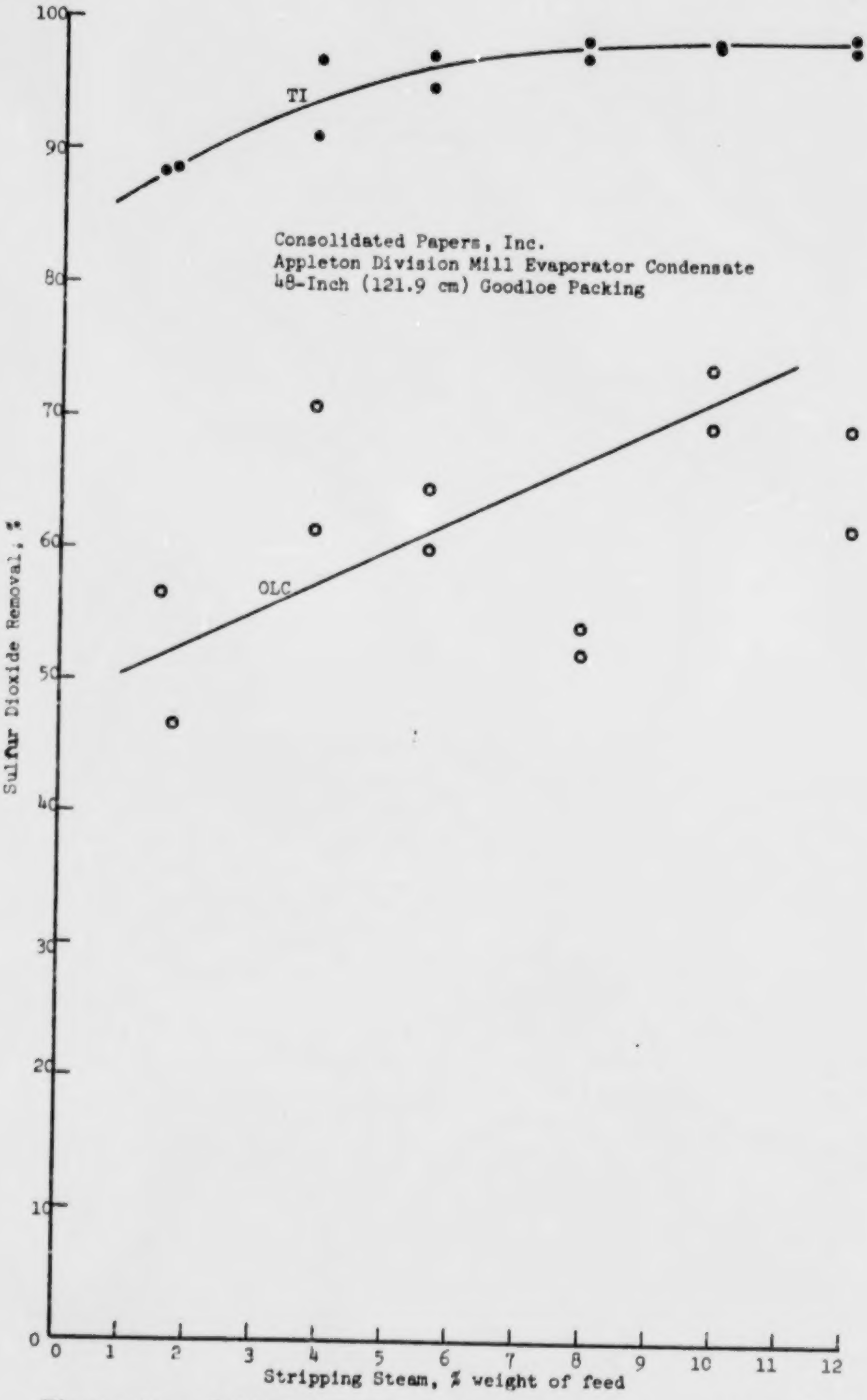


Figure 11. Sulfur dioxide removal vs. stripping steam used — Consolidated Papers, Inc. — 48-inch (121.9 cm) packing

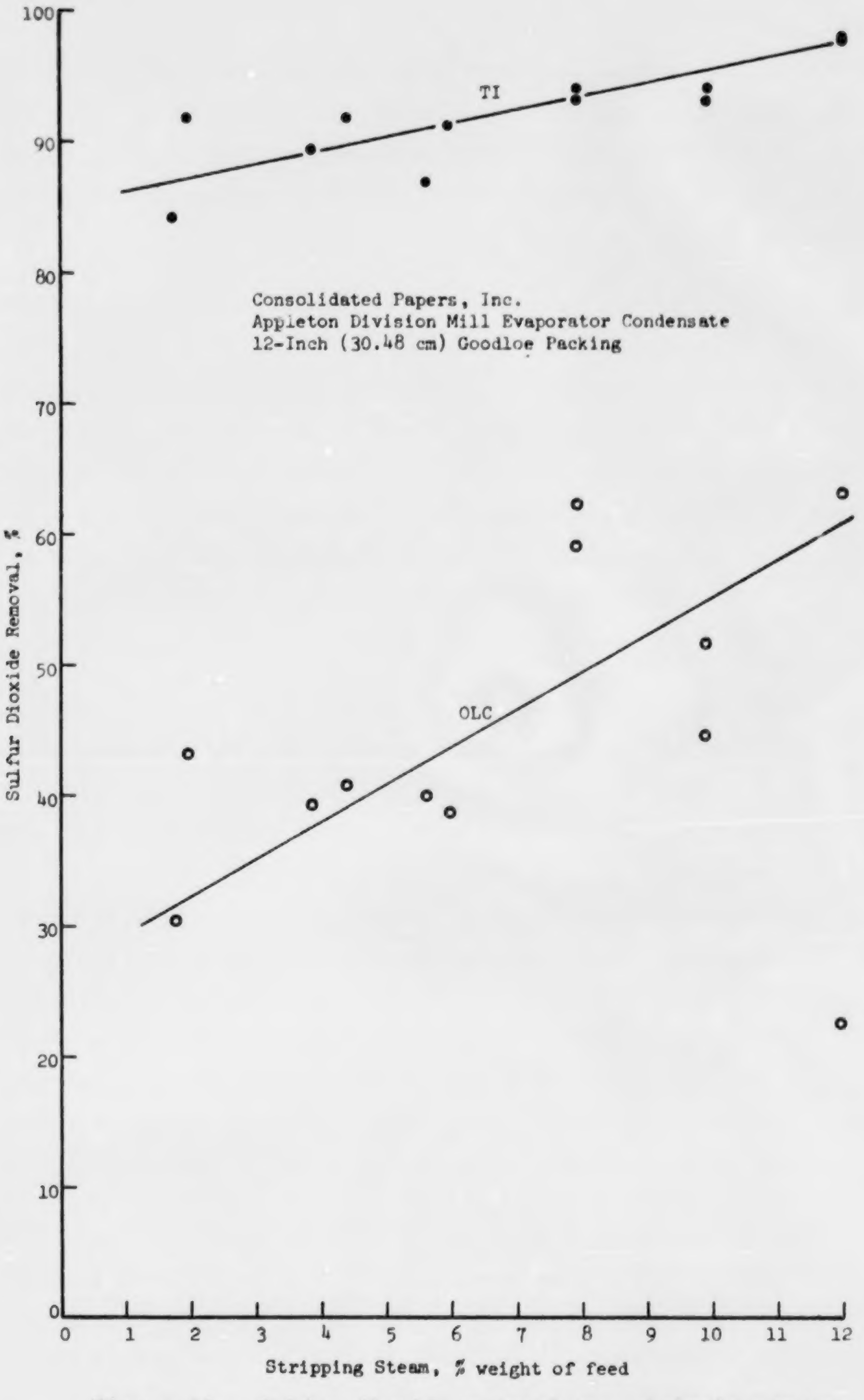


Figure 12. Sulfur dioxide removal vs. stripping steam used — Consolidated Papers, Inc. — 12-inch (30.48 cm) packing

there was a feed tank holding more than 1500 gallons (5670 liters) of blow gas condensate, and the feed entered the column at a temperature of 205°F (96.1°C). At Consolidated a 50-gallon (189 liters) feed drum was used, and the feed entered the column at a temperature of approximately 211°F (99.4°C).

Figures 5 and 6 show the percentage of methanol removal from Everett Mill's blow gas condensate as a direct straight-line function of the amount of stripping steam used. Note that none of the points are more than the equivalent of 5% methanol removal away from the line drawn, and both lines go through zero. This indicates the trial runs were made under ideal operating conditions. Figures 7 and 8 show 90% or more SO_2 removal, when using 2% or more weight of feed stripping steam. The better than 99% SO_2 removal in Fig. 7 versus the poor results on Fig. 8 was due to the following:

1. When the feed entered the column at 205°F (96.1°C), less than 2% by weight of feed stripping steam was not adequate to overcome the column heat losses and sensible heat required to raise the liquid in the column to its bubble point and effectively strip out the SO_2.
2. The data plotted in Fig. 7 were the result of samples analyzed immediately after they had been taken. Analyses in Fig. 8 were conducted hours or even the following day after the samples were taken. The free SO_2 shown in Fig. 8 was believed to be that regenerated from SO_2-OLC which was not removed. This was verified in future runs. SO_2-OLC became an important part of the analyses from August, 1971 to date.

The clusters of points in Fig. 6 at 3 and 6% by weight of feed stripping steam showed very little benefit derived from increasing column packing height. At 10% stripping steam rate some advantage was shown by increasing column height. Compare straight-line points in Fig. 5 and 6. However, it was doubtful that the increase would justify the additional construction costs.

Figures 9 and 10 show the percentage of methanol removal from the Consolidated Mill evaporator condensate. The points were very widely scattered, and the lines were discretely drawn. On Fig. 9 the two zero points were neglected as being bad data. The line was drawn keeping as many points on or near it as possible and an equal number on either side. Note that neither line on Fig. 9 and 10 goes through zero. This indicated the bubble point of our feed was probably exceeded and it partially vaporized in the preheater. Figures 11 and 12 show the percentage SO_2 removal of both TI and OLC. The SO_2-TI removal was similar to that shown for Scott in Fig. 8. The analyses were done in The Institute of Paper Chemistry laboratory hours or days after the samples were taken. An important fact shown in Fig. 11 and 12 was that no more than 75% of the SO_2-OLC was removed. Similar work on Scott's blow gas condensate showed 90+% SO_2-OLC consistently being removed. The difference was attributed to the SO_2-OLC in Consolidated Mill's evaporator condensate as the result of residual spent sulfite liquor removed from the evaporator by the condensate in the washing cycle. This SO_2-OLC was much more firmly combined.

This concluded the steam stripping experimental portion of this project. These data can assist any pulp and paper company interested in steam stripping sulfite mill evaporator condensate with their design, construction, and operation of a steam stripping system. The pilot plant also was in a position, with Consolidated Papers, Inc.'s approval, to test individual mill's evaporator condensates under predetermined operating conditions.

Fractionation

During the steam stripping runs the condensed overheads from the steam stripping column were fed into the fractionation column. Methanol and furfural crudes were recovered. Balances based on gas chromatographic analyses of the steam stripping column's feeds and condensed overheads are given in Tables 5 and 6. From the methanol balance, Table 5 methanol analyses showed 4.196 lb (1.90 kg) to be in the condensed

Table 5. METHANOL BALANCE STEAM STRIPPING RUNS
9-11-72 to 9-20-72

9-11-72

In Feed
4 hr (1.52 gpm) (60 min.) (8.33 lb/gal.) (0.00045) = 1.37 lb (0.622 kg)
In Overhead
4 hr (0.008) (60) (8.33) (0.027) = 0.43 lb (0.195 kg)
% Recovery = (0.43/1.37) 100 = 31.4%

9-12-72

In Feed
4 (1.368) (60) (8.33) (0.000575) = 1.575 lb (0.715 kg)
In Overhead
4 (0.038) (60) (8.33) (0.00385) = 0.290 lb (0.132 kg)
% Recovery = (0.290/1.575) 100 = 18.6%

9-12-72

In Feed
4 (1.215) (60) (8.33) (0.00045) = 1.095 lb (0.497 kg)
In Overhead
4 (0.049) (60) (8.33) (0.0030) = 0.290 lb (0.132 kg)
% Recovery = (0.290/1.095) 100 = 26.5%

9-14-72

In Feed
4 (0.76) (60) (8.33) (0.00055) = 0.84 lb (0.381 kg)
In Overhead
4 (0.045) (60) (8.33) (0.00355) = 0.32 lb (0.145 kg)
% Recovery = (0.32/0.84) 100 = 38.0%

9-14-72

In Feed
4 (0.608) (8.33) (60) (0.000725) = 0.88 lb (0.399 kg)
In Overhead
4 (0.043) (8.33) (60) (0.004225) = 0.36 lb (0.163 kg)
% Recovery = (0.36/0.88) 100 = 41.2%

Table 5 (cont'd). METHANOL BALANCE STEAM STRIPPING RUNS
9-11-72 to 9-20-72

9-15-72

In Feed
4 (0.502) (8.33) (60) (0.000575) = 0.578 lb (0.263 kg)
In Overhead
4 (0.0409) (8.33) (60) (0.00335) = 0.328 lb (0.149 kg)
% Recovery = (0.328/0.578) 100 = 56.8%

9-18-72

In Feed
4 (1.52) (8.33) (60) (0.00094) = 2.74 lb (1.245 kg)
In Overhead
4 (0.047) (8.33) (60) (0.0043) = 0.405 lb (0.184 kg)
% Recovery = (0.405/2.74) 100 = 14.8%

9-18-72

In Feed
4 (1.368) (8.33) (60) (0.00056) = 1.53 lb (0.695 kg)
In Overhead
4 (0.045) (8.33) (60) (0.00354) = 0.318 lb (0.144 kg)
% Recovery = (0.318/1.53) 100 = 20.8%

9-19-72

In Feed
2 (1.140) (8.33) (60) (0.00061) = 0.695 lb (0.316 kg)
In Overhead
2 (0.050) (8.33) (60) (0.00424) = 0.212 lb (0.096 kg)
% Recovery = (0.212/0.695) 100 = 30.5%

9-19-72

In Feed
2 (1.215) (8.33) (60) (0.00056) = 0.680 lb (0.309 kg)
In Overhead
2 (0.057) (8.33) (60) (0.00364) = 0.207 lb (0.094 kg)
% Recovery = (0.207/0.680) 100 = 30.5%

9-19-72

In Feed
4 (0.76) (8.33) (60) (0.00035) = 0.532 lb (0.242 kg)
In Overhead
4 (0.046) (8.33) (60) (0.00270) = 0.248 lb (0.113 kg)
% Recovery = (0.248/0.532) 100 = 46.7%

Table 5 (cont'd). METHANOL BALANCE STEAM STRIPPING RUNS
9-11-72 to 9-20-72

9-20-72

In Feed
4 (0.608) (8.33) (60) (0.000725) = 0.881 lb (0.40 kg)
In Overhead
4 (0.050) (8.33) (60) (0.00412) = 0.412 lb (0.187 kg)
% Recovery = (0.412/0.881) 100 = 46.8%

9-20-72

In Feed
4 (0.502) (8.33) (60) (0.0007) = 0.704 lb (0.32 kg)
In Overhead
4 (0.051) (8.33) (60) (0.00369) = 0.376 lb (0.171 kg)
% Recovery = (0.374/0.704) 100 = 53.5%

Total methanol in overhead

0.430 lb
0.290 lb
0.290 lb
0.320 lb
0.360 lb
0.328 lb
0.405 lb
0.318 lb
0.212 lb
0.207 lb
0.248 lb
0.412 lb
0.376 lb

4.196 lb (1.90 kg)

Collected — 4.3 lb (1.95 kg)

Table 6. FURFURAL BALANCE STEAM STRIPPING RUNS
9-11-72 to 9-20-72

9-11-72

In Feed
4 hr (1.52 gpm) (60 min.) (8.33 lb/gal.) (0.0001) = 0.30 lb (0.136 kg)
In Overhead
4 (0.008) (60) (8.33) (0.0012) = 0.019 lb (0.0086 kg)
% Recovery = (0.019/0.30) 100 = 6.3%

9-12-72

In Feed
4 (1.368) (60) (8.33) (0.00025) = 0.684 lb (0.310 kg)
In Overhead
4 (0.038) (60) (8.33) (0.00155) = 0.117 lb (0.053 kg)
% Recovery = (0.117/0.684) 100 = 17.1%

9-12-72

In Feed
4 (1.215) (60) (8.33) (0.00020) = 0.486 lb (0.221 kg)
In Overhead
4 (0.049) (60) (8.33) (0.001385) = 0.133 lb (0.0604 kg)
% Recovery = (0.133/0.486) 100 = 27.4%

9-14-72

In Feed
4 (0.76) (60) (8.33) (0.000175) = 0.267 lb (0.121 kg)
In Overhead
4 (0.045) (60) (8.33) (0.001) = 0.090 lb (0.0408 kg)
% Recovery = (0.090/0.267) 100 = 33.7%

9-14-72

In Feed
4 (0.608) (60) (8.33) (0.0002) = 0.243 lb (0.110 kg)
In Overhead
4 (0.043) (60) (8.33) (0.00105) = 0.089 lb (0.0404 kg)
% Recovery = (0.089/0.243) 100 = 36.8%

Table 6 (cont'd). FURFURAL BALANCE STEAM STRIPPING RUNS 9-11-72 to 9-20-72

9-15-72

In Feed
4 (0.502) (60) (8.33) (0.0002) = 0.201 lb (0.0912 kg)
In Overhead
4 (0.049) (60) (8.33) (0.000925) = 0.0906 lb (0.0411 kg)
% Recovery = (0.0906/0.201) 100 = 45.0%

9-18-72

In Feed
4 (1.52) (60) (8.33) (0.000265) = 0.772 lb (0.351 kg)
In Overhead
4 (0.047) (60) (8.33) (0.001335) = 0.126 lb (0.0571 kg)
% Recovery = (0.126/0.772) 100 = 16.3%

9-18-72

In Feed
4 (1.368) (60) (8.33) (0.000175) = 0.478 lb (0.217 kg)
In Overhead
4 (0.045) (60) (8.33) (0.000885) = 0.0795 lb (0.0361 kg)
% Recovery = (0.0795/0.478) 100 = 16.6%

9-19-72

In Feed
2 (1.140) (60) (8.33) (0.00015) = 0.171 lb (0.0776 kg)
In Overhead
2 (0.050) (60) (8.33) (0.00091) = 0.0455 lb (0.0207 kg)
% Recovery = (0.0455/0.171) 100 = 27.6%

9-19-72

In Feed
2 (1.215) (60) (8.33) (0.0002) = 0.243 lb (0.110 kg)
In Overhead
2 (0.057) (60) (8.33) (0.00071) = 0.0404 lb (0.0183 kg)
% Recovery = (0.0404/0.243) 100 = 16.6%

9-19-72

In Feed
4 (0.76) (60) (8.33) (0.000125) = 0.190 lb (0.0862 kg)
In Overhead
4 (0.046) (60) (8.33) (0.000635) = 0.0583 lb (0.0265 kg)
% Recovery = (0.0583/0.190) 100 = 30.7%

Table 6 (cont'd). FURFURAL BALANCE STEAM STRIPPING RUNS
9-11-72 to 9-20-72

9-20-72

In Feed
4 (0.608) (60) (8.33) (0.0001) = 0.122 lb (0.0554 kg)
In Overhead
4 (0.050) (60) (8.33) (0.000825) = 0.0825 lb (0.0374 kg)
% Recovery = (0.0825/0.122) 100 = 67.6%

9-20-72

In Feed
4 (0.502) (60) (8.33) (0.00015) = 0.151 lb (0.0685 kg)
In Overhead
4 (0.051) (60) (8.33) (0.000825) = 0.084 lb (0.0381 kg)
% Recovery = (0.084/0.151) 100 = 55.6%

Total furfural in overhead

0.019 lb
0.117 lb
0.133 lb
0.090 lb
0.089 lb
0.091 lb
0.126 lb
0.080 lb
0.046 lb
0.040 lb
0.058 lb
0.082 lb
0.084 lb

1.055 lb (0.479 kg)

Collected — 0.925 lb (0.419 kg)

overheads. The methanol recovered was 4.3 lb (1.95 kg). Although analyses showed it to be in the 85 to 90% by weight range, the bubble point and specific gravity indicated a 95+% by weight methanol crude. From the furfural balance, Table 6 furfural analyses showed 1.055 lb (0.48 kg) to be in the condensed overheads. Furfural recovered was 0.925 lb (0.42 kg). Analyses showed it to be in the 84 to 92% by weight range. This work was done before we developed our gas chromatographic programs for analyzing high purity methanol, ethanol, ethyl acetate, methyl acetate, and furfural products. No sample of the fractionation column bottoms contained even trace quantities of methanol or furfural. There was zero pressure drop from the feed port to the bottom of the fractionation column indicating this column was grossly oversized. No attempt was made to preheat the condensate to its bubble point. The reboiler and condenser were more than adequate. The work at Scott Paper Company utilized steam stripping and fractionation on the evaporator condensate before it was pumped through the activated carbon columns, and the fractionation column was the piece of equipment that limited the pilot plant capacity to processing less than 1/2 gpm (1.9 liters per minute) of the condensate. No attempt was made to optimize the size of the fractionation column, since the project priority was shifted to getting activated carbon adsorption and regeneration data.

Activated Carbon Adsorption

After the steam stripping work was completed, steam stripped evaporator condensate was processed through the activated carbon columns at the rate of 1 gpm (3.8 liters per minute). Six percent by weight of feed stripping steam was used. The overhead vapors were condensed and processed through the fractionation column. The steam stripped evaporator condensate was processed as shown in Fig. 2 (p. 20).

The first run was made October 9, 1972. Efforts were concentrated on the steam stripping and activated carbon adsorption columns. Almost 100 samples were taken over a 16-hour period to effectively study these unit operations. Hundreds of separate analyses were made on these samples. The data accumulated have been plotted in Fig. 13 to 22. Figure 13 shows the acetic acid concentrations in the feed to and in the bottom liquid from the steam stripping column. Interestingly, the acetic acid concentration was consistently lower than that in the feed, most of the time much lower than can be accounted for by the 6% stripping steam dilution. Since a darkening of color in the processed condensate was apparent, the acetic acid lost may be responsible in part for some of the polymerized material collected. No analytical effort has been made to verify or disprove this. Figure 14 shows the acetic acid concentrations of the feed to and effluent from the first activated carbon column. There was no acetic acid in the effluent for over 3 hours. From previous Scott work the breakthrough point had been calculated to occur after 2-3/4 hours. The increased time may have been due to lower concentrations of acetic acid in the feed. Note that after 5 hours there was more acetic acid in the effluent than in the feed. Then, after 8 hours the carbon was adsorbing it again. During this period the feed concentration was rising. After 13 hours there was more in the effluent once again. Figure 15 demonstrates some analytical problems. Up until this time one injection of the sample was made into the gas chromatograph. Since the acetic acid concentrations of the samples were relatively close, no problems had arisen. Now injections of samples with acetic acid concentrations varying from 1% or better were mixed with those containing no acetic acid. Since it was illogical that the acetic acid would break through both activated carbon columns at the same time, two of the effluent samples fortunately saved were checked. They showed no acetic acid, ith the improved injection procedure, so it was concluded the acetic acid shown previously was coming from the injection needle and/or gas chromatograph column. Poropak Q columns require some column conditioning with acetic acid. Similar experiences were encountered at Scott. All later quantitative work on the gas chromatograph utilized 3 sample injections. With this modification of analytical procedure it could be shown that little or no acetic acid was adsorbed in the first 4 hours because it

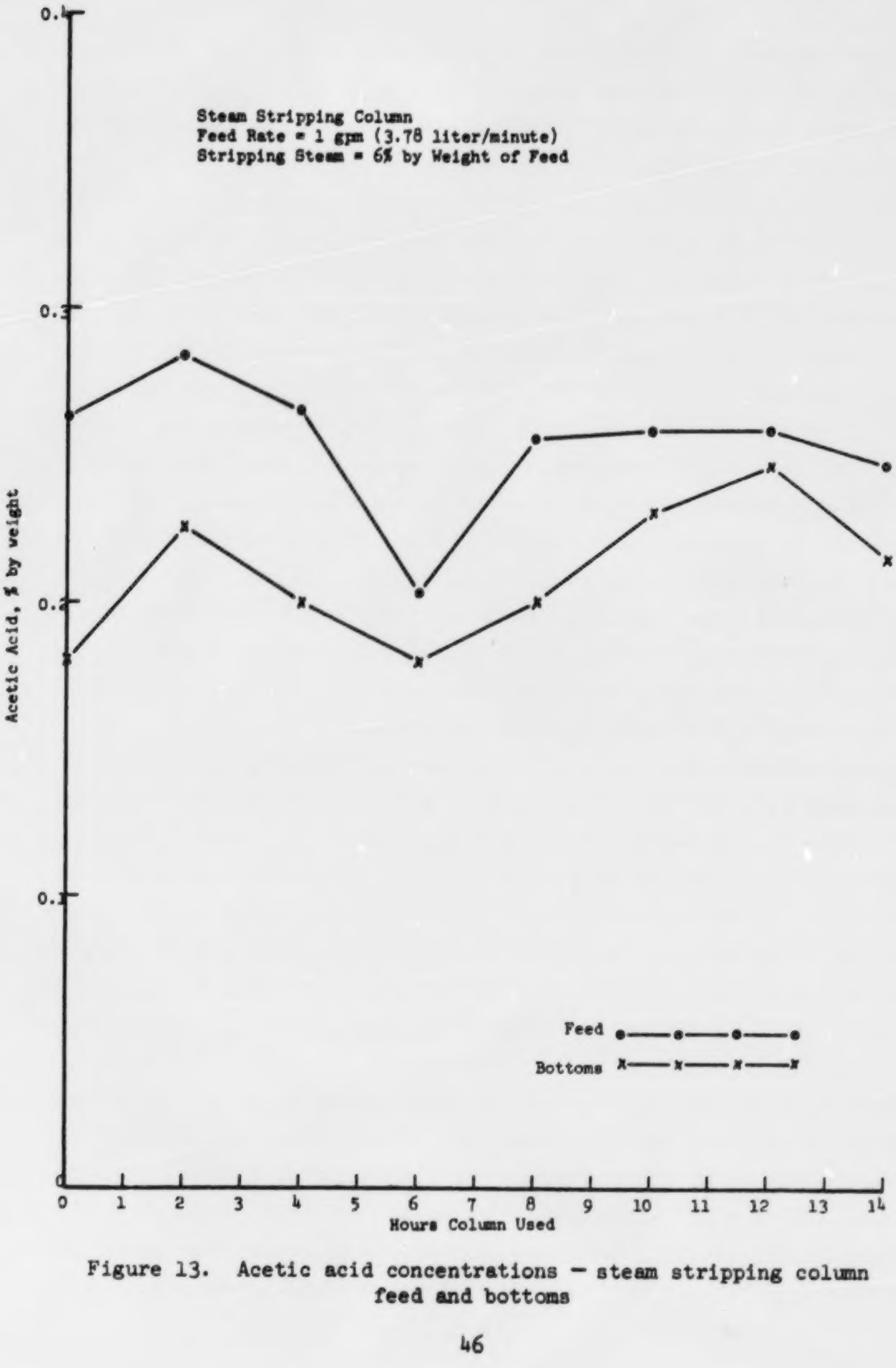


Figure 13. Acetic acid concentrations — steam stripping column feed and bottoms

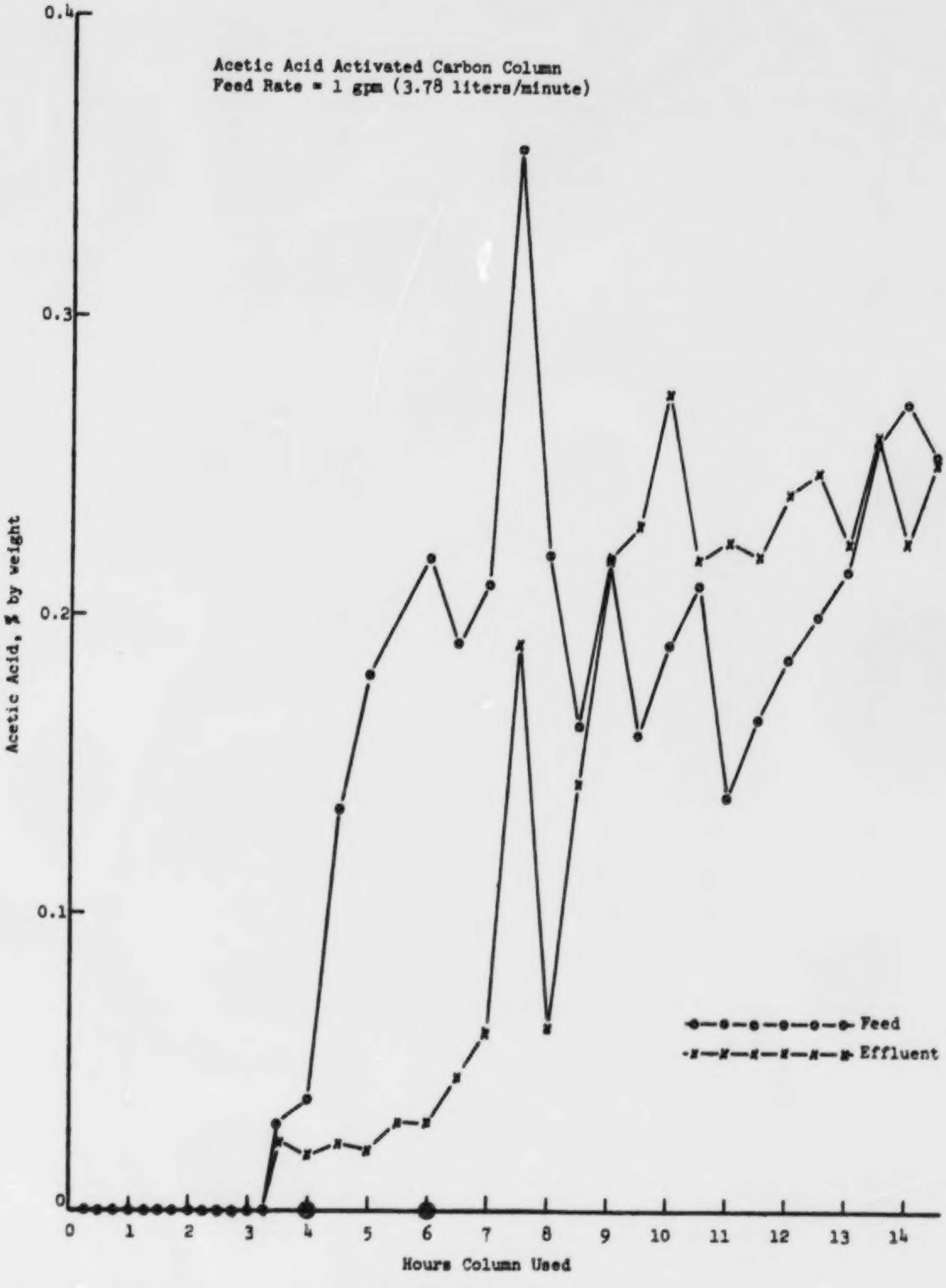


Figure 14. Acetic acid concentrations — furfural activated carbon column feed and effluent

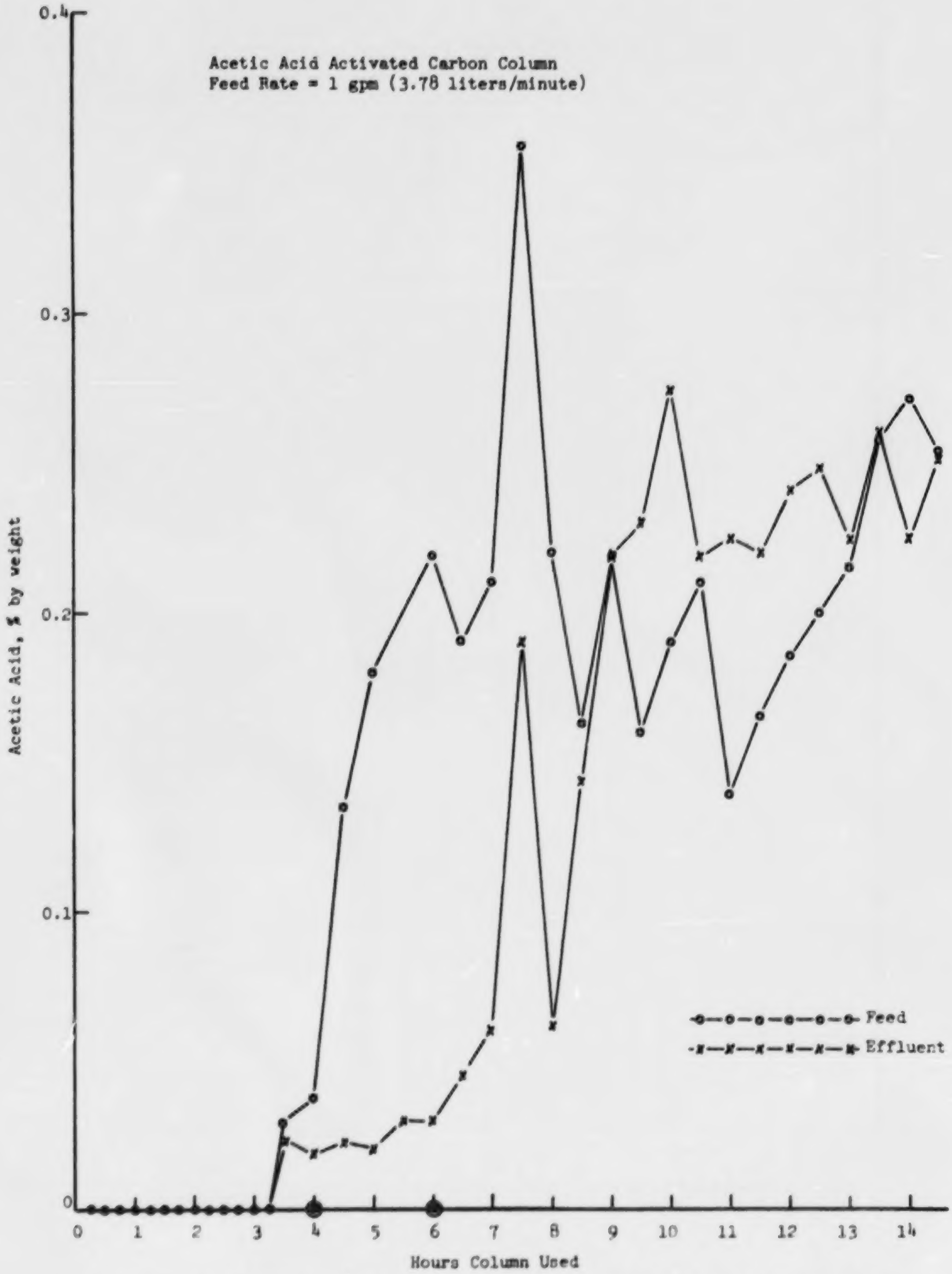


Figure 15. Acetic acid concentrations — acetic acid activated carbon column feed and effluent

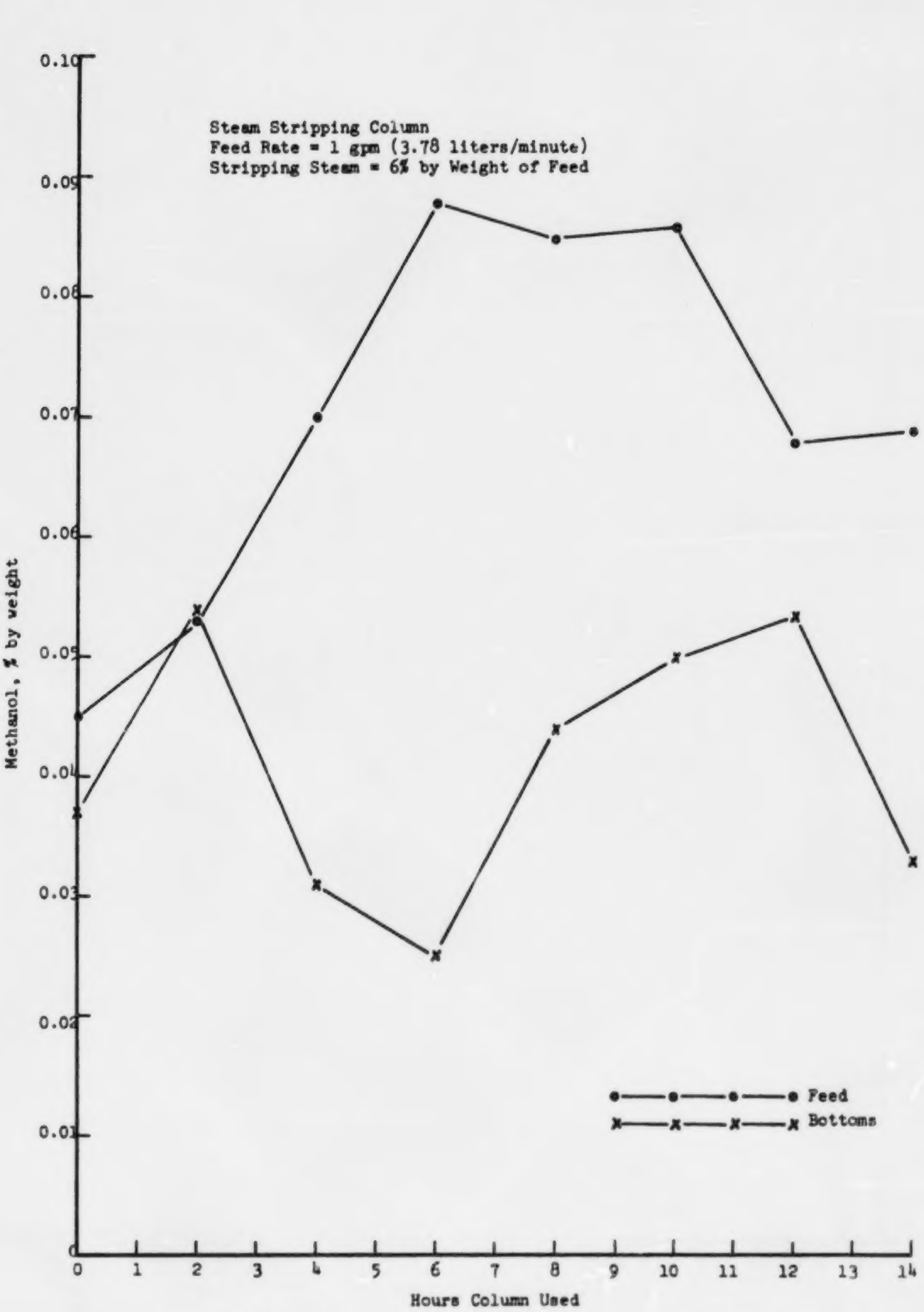


Figure 16. Methanol concentration — steam stripping column feed and bottoms

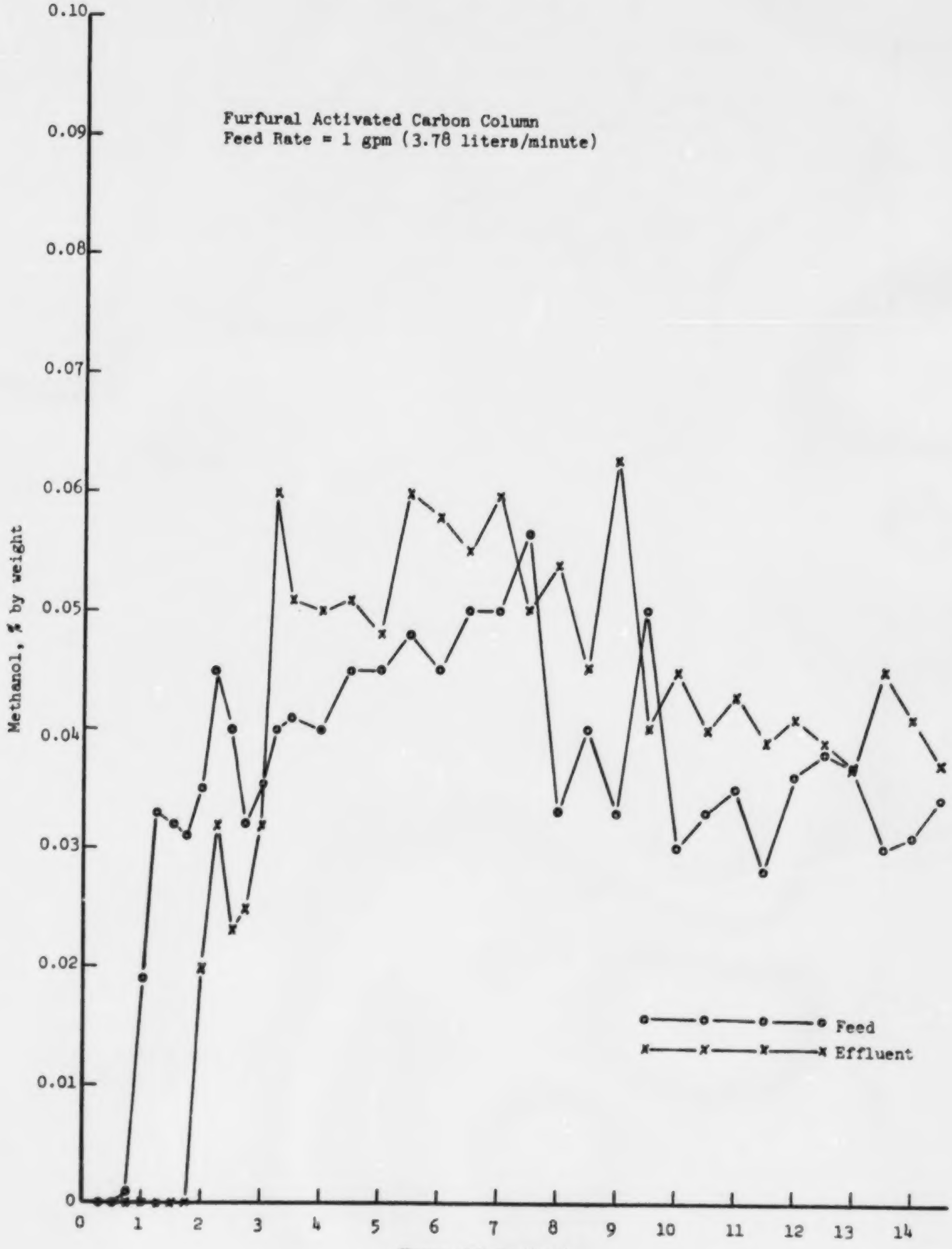


Figure 17. Methanol concentration — furfural activated carbon column feed and effluent

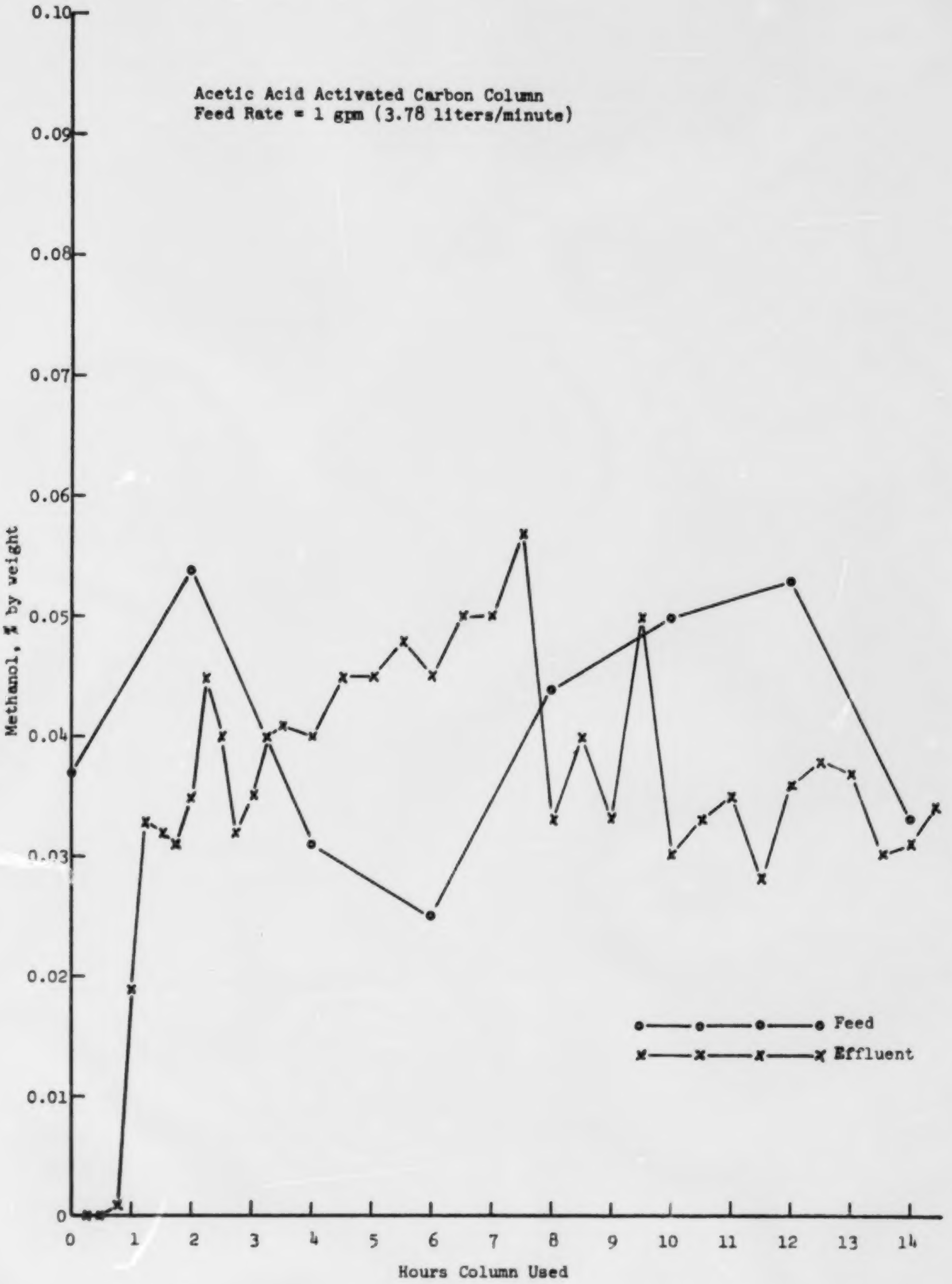


Figure 18. Methanol concentration — acetic acid activated carbon column feed and effluent

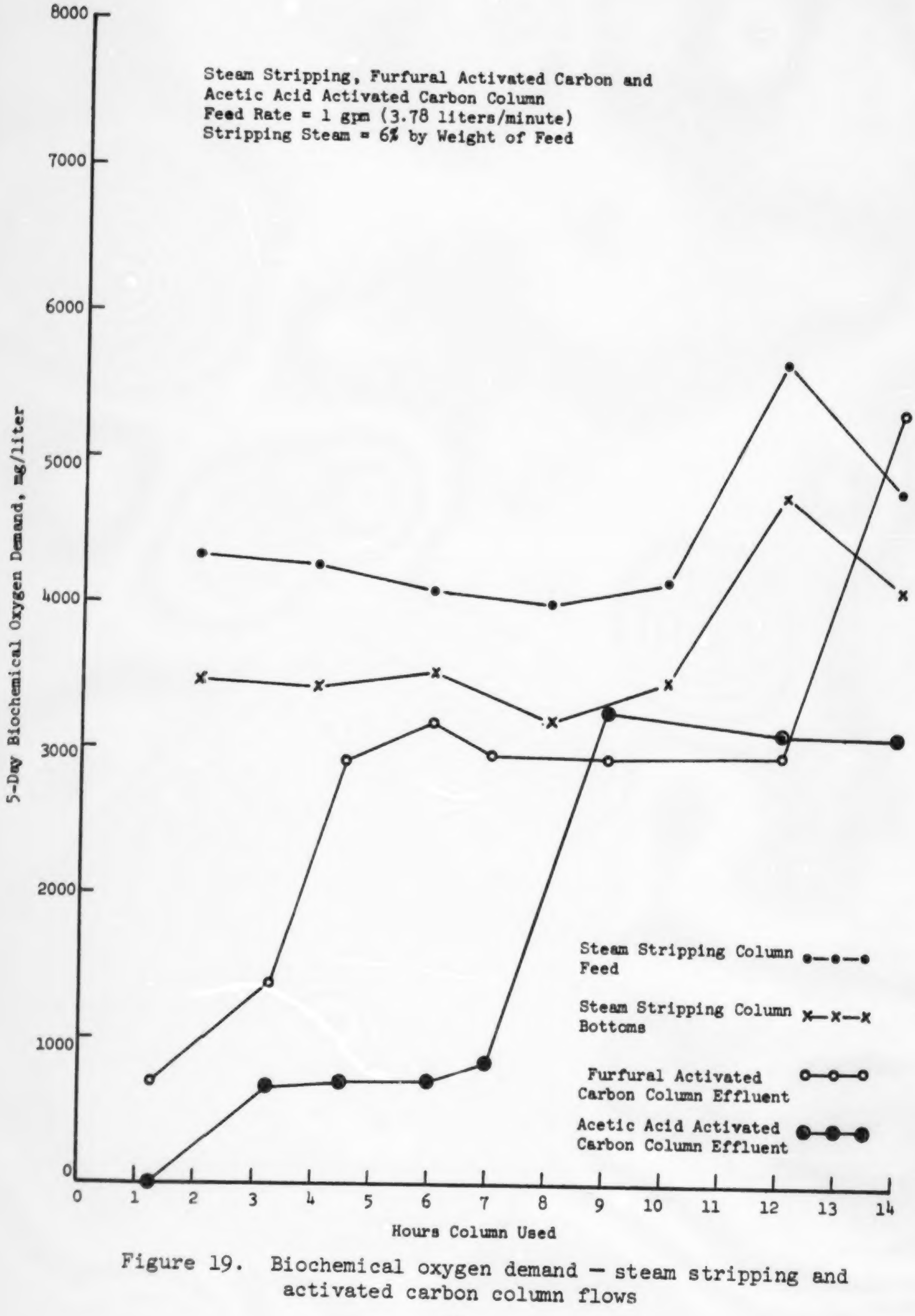


Figure 19. Biochemical oxygen demand — steam stripping and activated carbon column flows

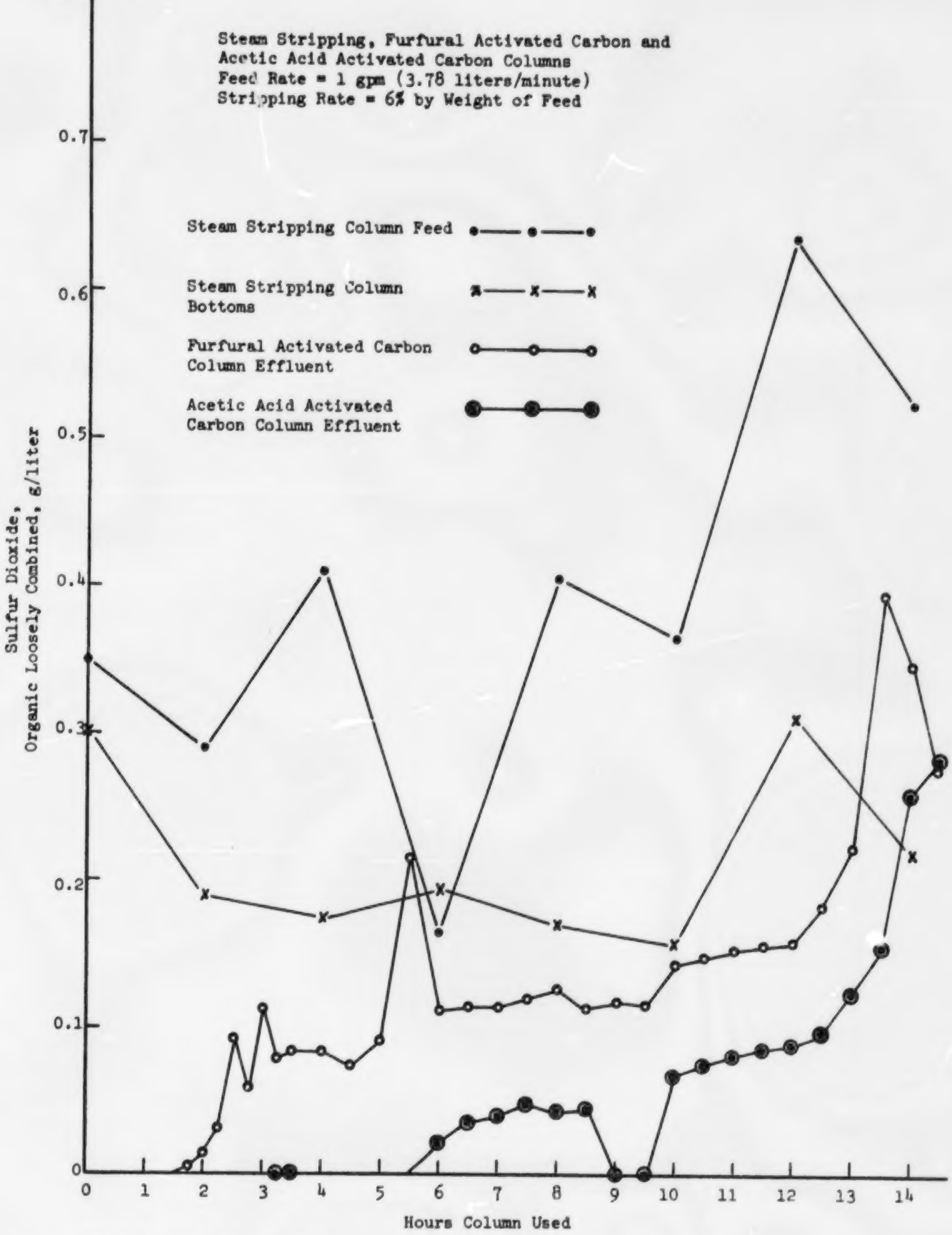


Figure 20. Organic loosely combined sulfur dioxide concentrations — steam stripping and activated carbon column flows

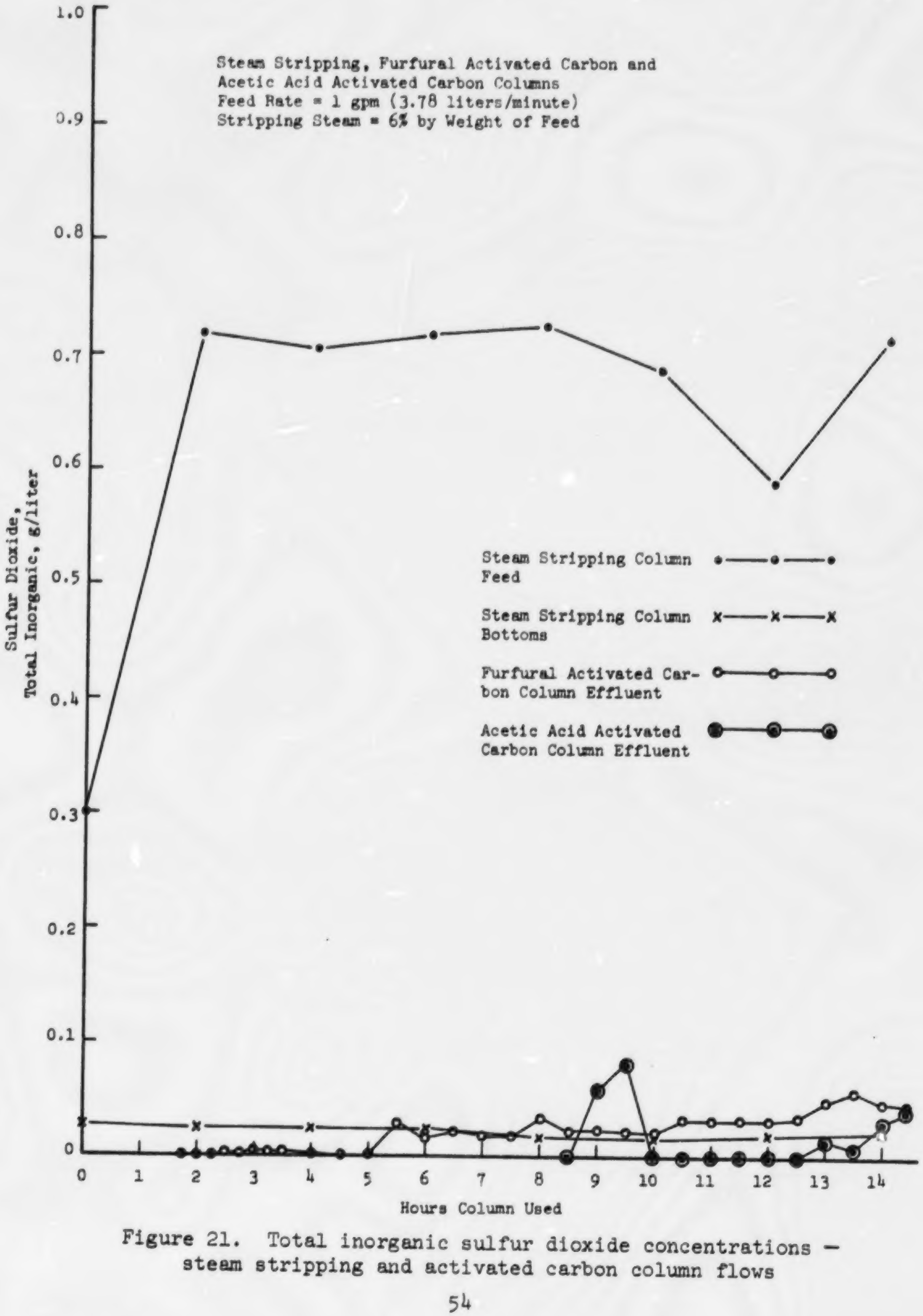


Figure 21. Total inorganic sulfur dioxide concentrations – steam stripping and activated carbon column flows

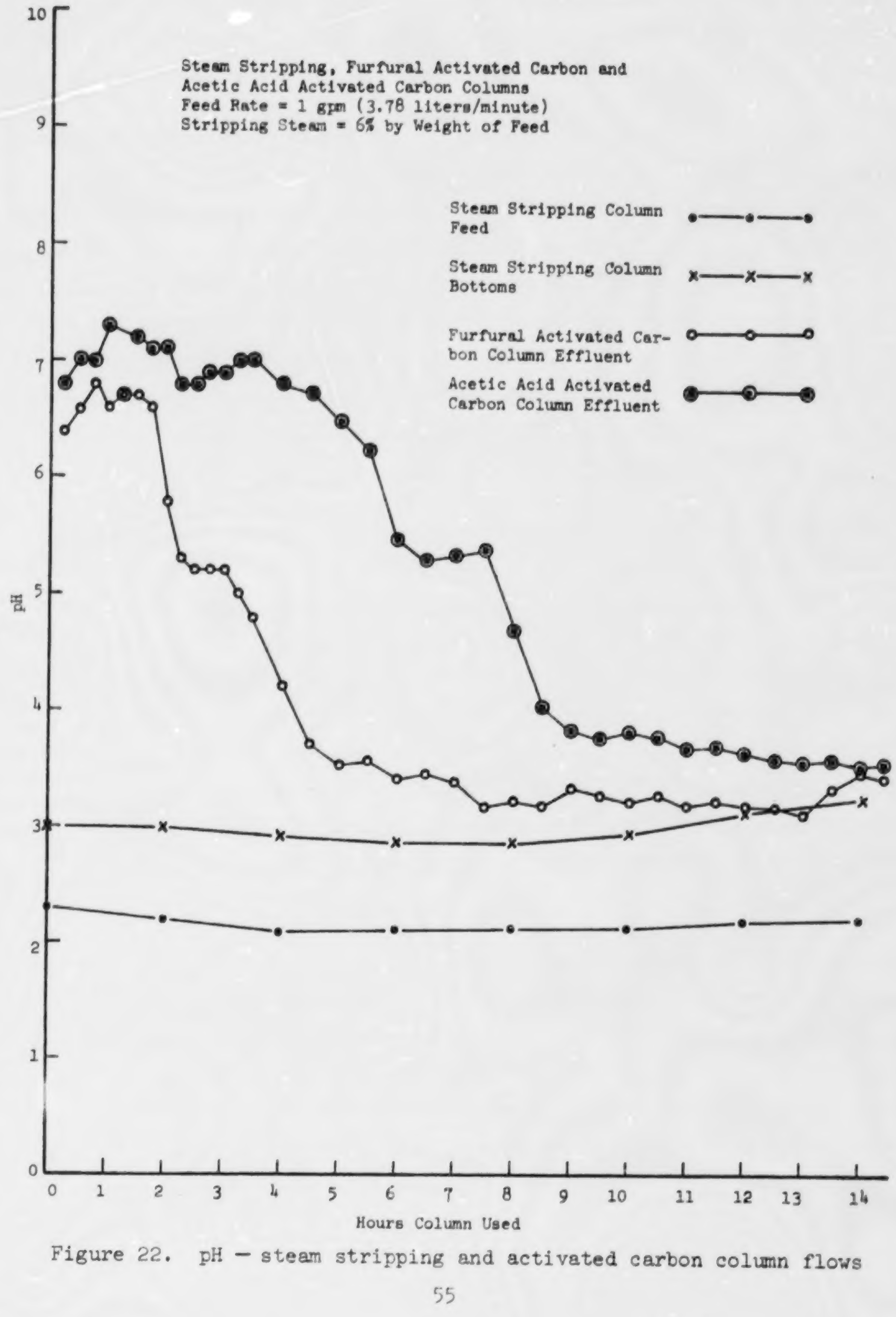


Figure 22. pH — steam stripping and activated carbon column flows

had been adsorbed on the previous column. For the next five hours acetic acid was being absorbed, and in the final 5 hours it was being pushed out of the carbon at a faster rate than it was being adsorbed.

The next three graphs, Fig. 16 to 18, show the methanol concentrations and are similar to the first four on acetic acid. About 50% of the methanol in the feed was expected to be removed by steam stripping. Figure 16 shows this was not always achieved. Since this was the first run with the activated carbon columns, too much effort was placed on their operation, and the steam stripping was not as efficient as it should have been. Figure 17 shows that methanol goes through activated carbon quickly with little adsorption. It also absorbs and readsorbs depending on feed concentrations. Figure 18 is similar to Fig. 17, but deals with the second carbon column.

Figures 19 to 22 are composite graphs covering the BOD and sulfur dioxide analyses of the samples, as well as their pH. Figure 19 shows the BOD reduction over the 14-hour operating period. The 700 mg/liter range indicates the BOD of the residual methanol. The 3000 mg/liter range is indicated for the acetic acid and residual methanol, the 3500 to 4800 range includes acetic acid, residual methanol, residual furfural, and some polymerized material, and the 4000 to 5700 range contains all the acetic acid, methanol, furfural, and other materials. Any commercial acetic acid activated carbon adsorption unit that will be, or has been recommended, would be designed on the basis of 2 1/2 to 3 hours data.

Figures 23 through 28 represent data obtained during repeats of the 14-hour run, except the activated carbon column in which the acetic acid was adsorbed had its carbon regenerated using ethanol. Since furfural had not broken through the activated carbon in the first column, its use was continued. Figure 23 shows the acetic acid breaking through the column at about 3 hours operating time, not appreciably different from that of the virgin carbon indicating very good regeneration.

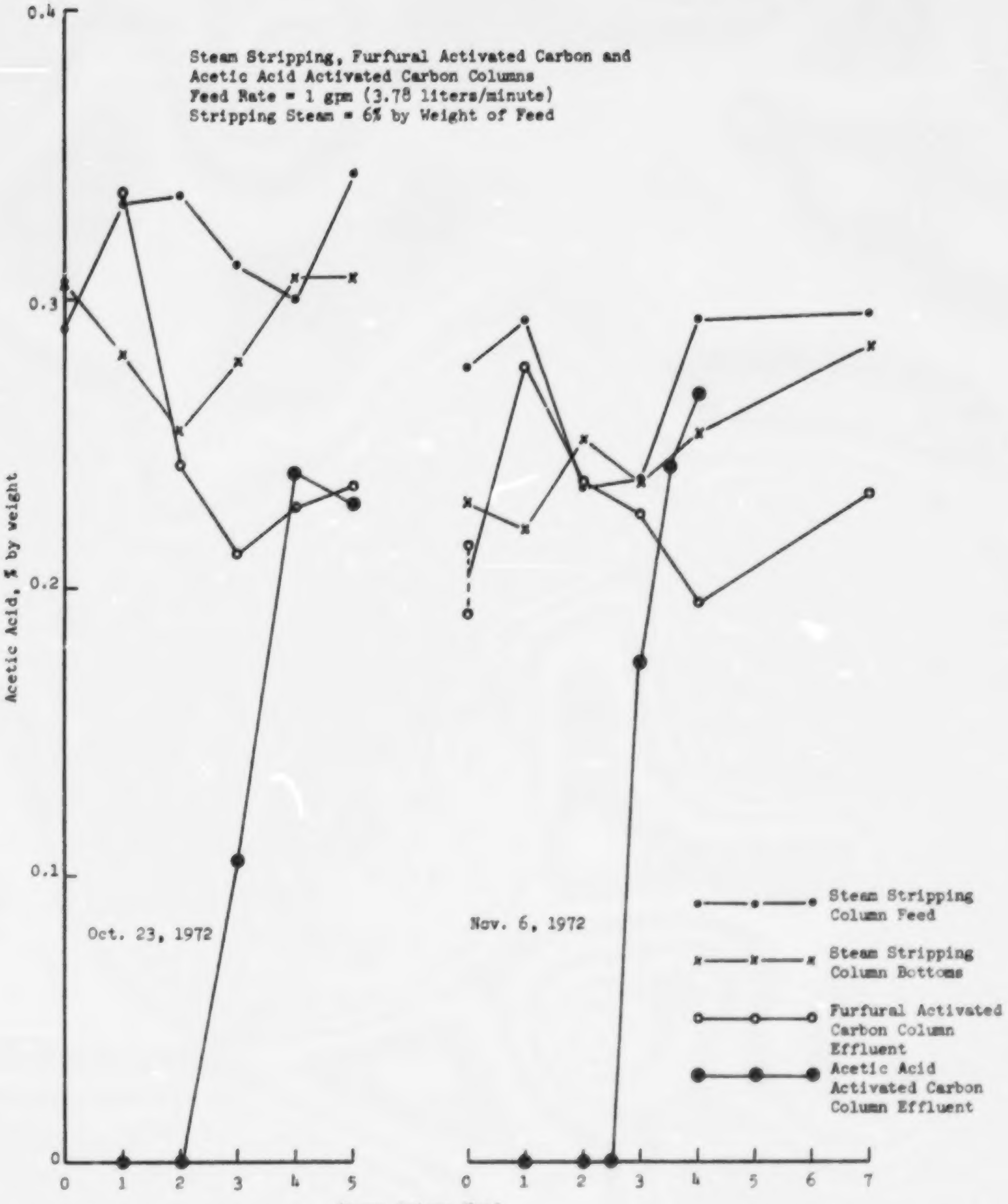


Figure 23. Acetic acid concentrations — steam stripping and activated carbon column flows using regenerated carbon

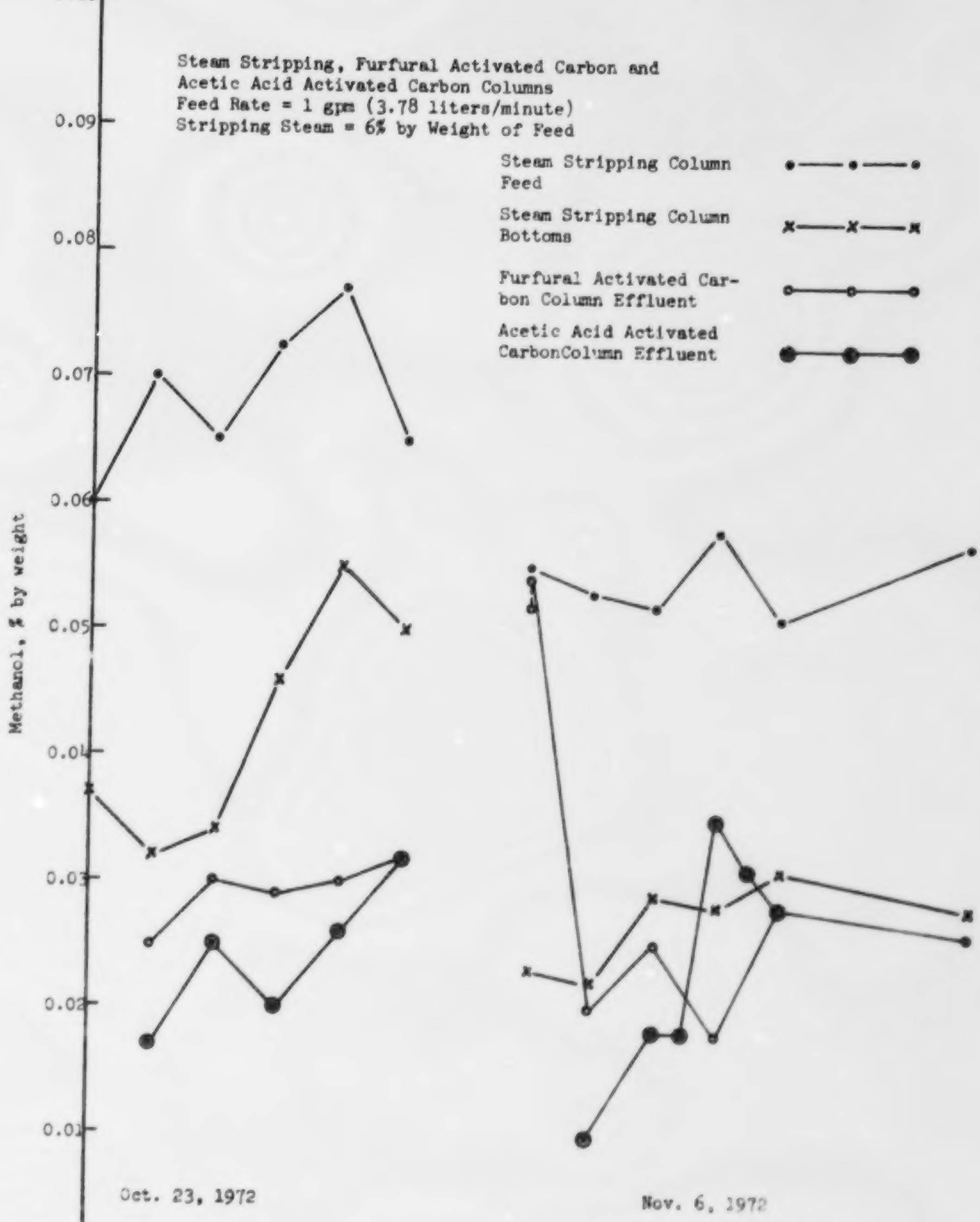


Figure 24. Methanol concentrations — steam stripping and activated carbon column flows using regenerated carbon

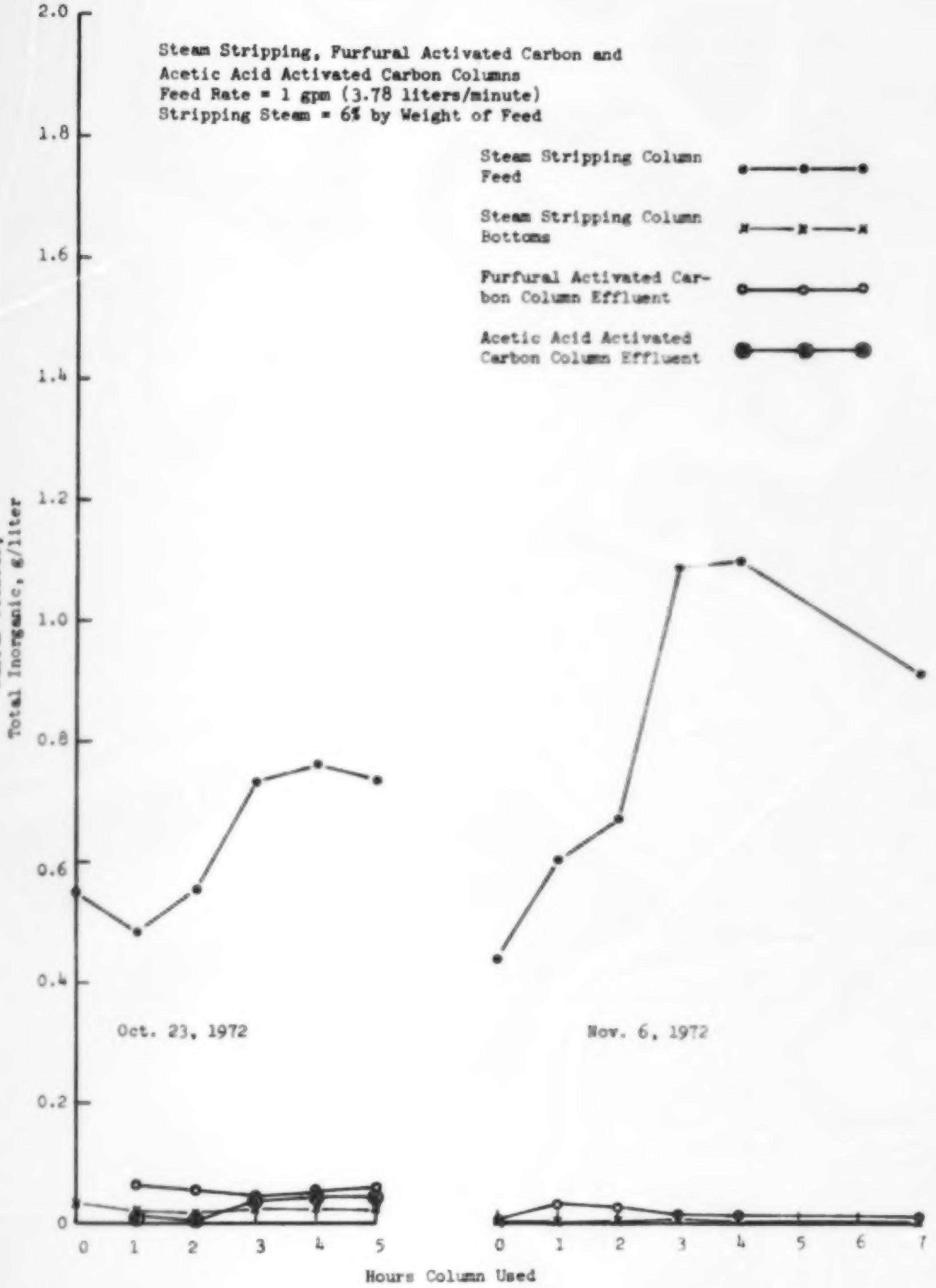


Figure 25. Total inorganic sulfur dioxide concentrations — steam stripping and activated carbon column flow using regenerated carbon

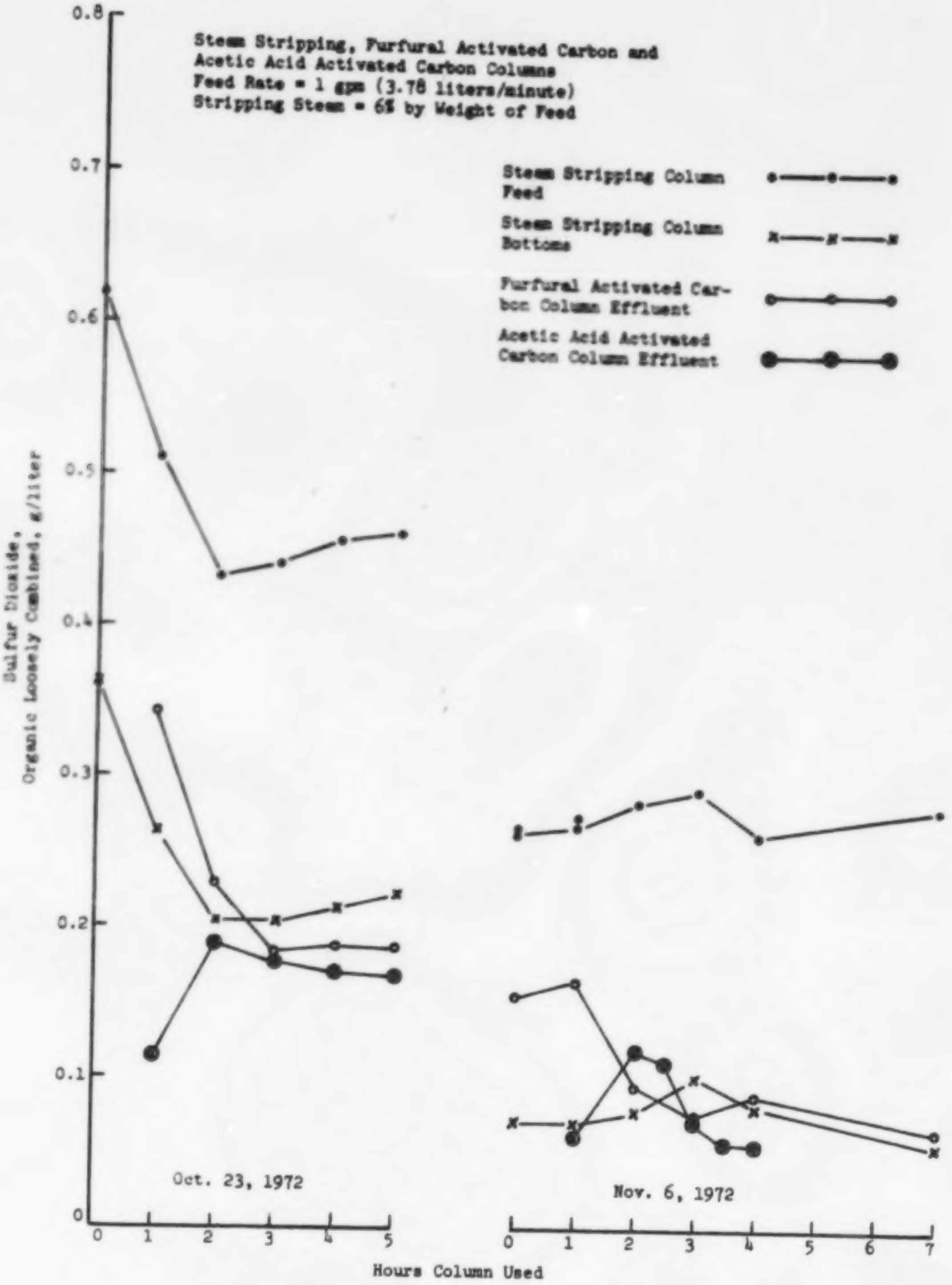


Figure 26. Organic loosely combined sulfur dioxide concentrations — steam stripping and activated carbon column flow using regenerated carbon

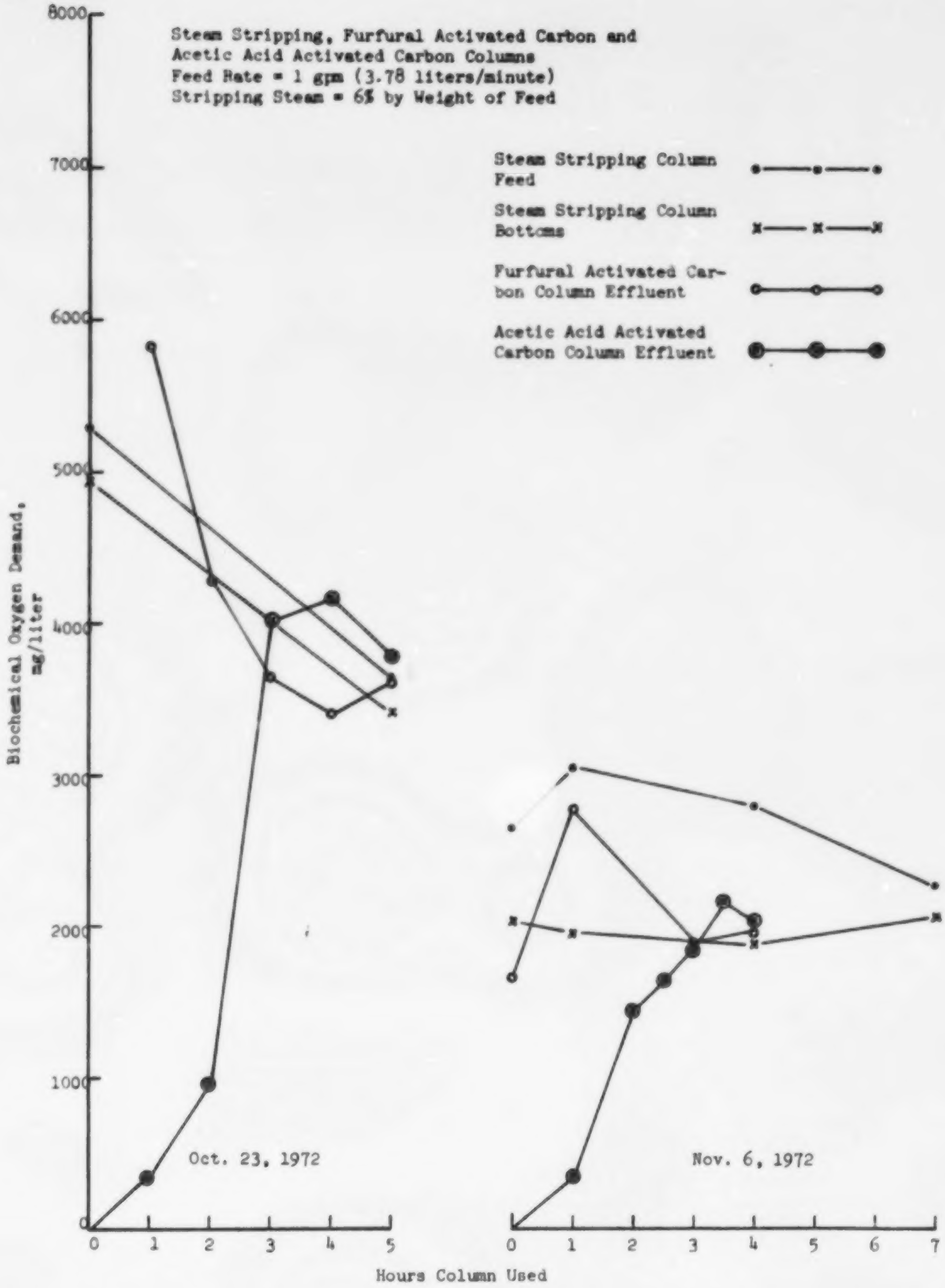


Figure 27. Biochemical oxygen demand — steam stripping and activated carbon column flow using regenerated carbon

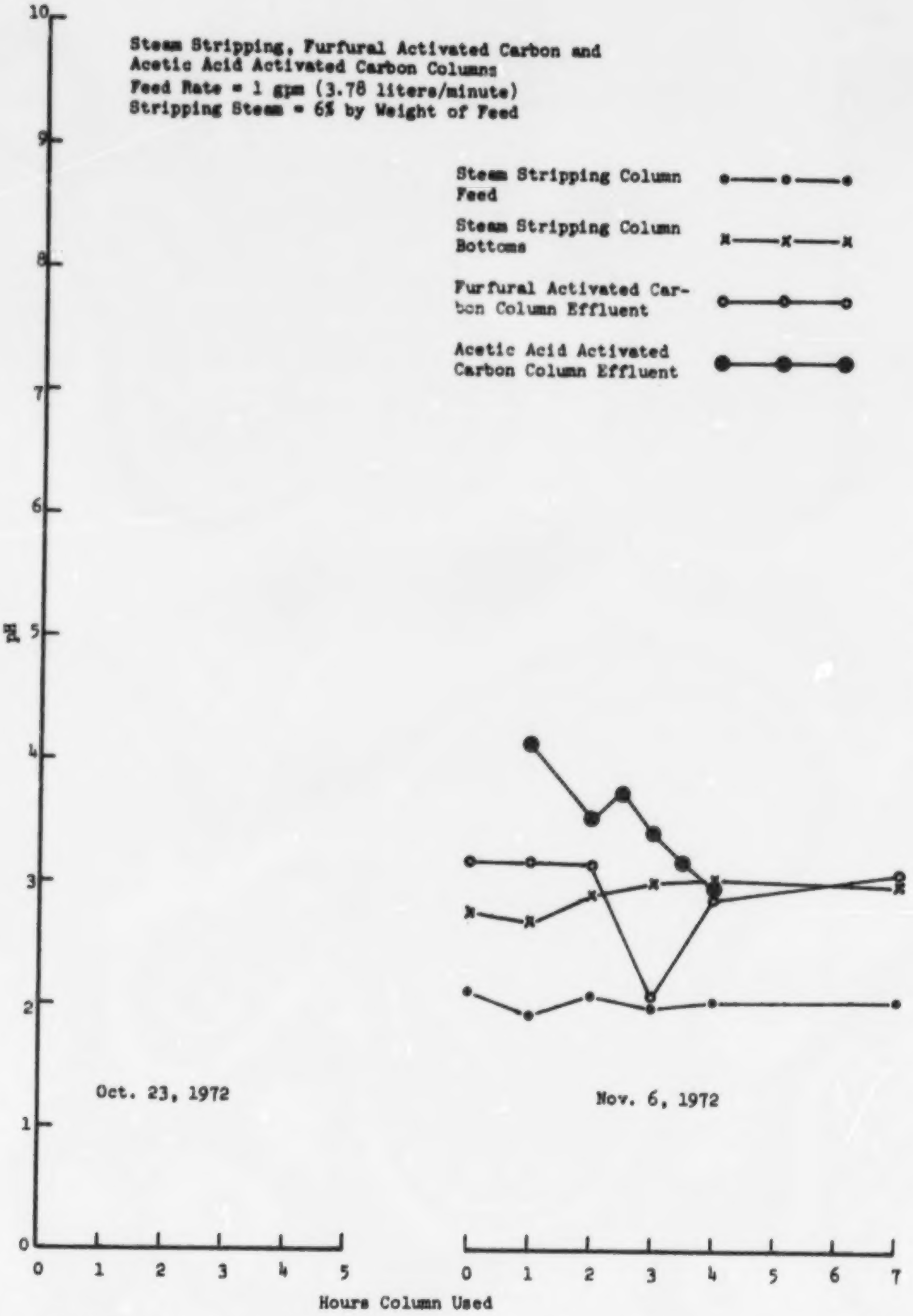


Figure 28. pH — steam stripping and activated carbon column flow using regenerated carbon

Figure 24 shows methanol being adsorbed in both activated carbon columns over the entire 5-hour operation on October 23, 1972. The run of November 6, 1972 was more normal. Since methyl acetate was recovered during regeneration, methanol reactions were possible as these chemicals were allowed to set in the column. Figure 27 is interesting in that no acetic acid appeared in the 2 and 2 1/2-hour samples, and yet the BOD is almost as high as that in the steam stripping column bottom liquor.

This BOD should be characterized in further studies. If the 700 mg/liter BOD range that has been attributed to residual methanol is a problem area of concern, remember that the steam stripping column was operated utilizing 6% by weight of feed stripping steam. Higher steam utilization will reduce the methanol. The effluent was to be recycled. Any recycle problems would have to be evaluated against the cost of using more stripping steam.

Two more regenerations of the carbon in the column adsorbing acetic acid were made, but no attempt was made for chemical recovery or material balances, since the multipoint recorder malfunctioned spoiling the 3rd regeneration cycle and 4th adsorption cycle. More than 5 weeks pilot plant operation time was lost, before this unit was repaired.

Since furfural had not broken through the carbon in the first activated carbon column, that carbon column and the steam stripping column were operated every day until a breakthrough did occur. This required 70 1/2 hours total operating time. Actually, the furfural was held in the column from October 9, 1972 until December 21, 1972. The data compiled in this belated recovery run was plotted in Fig. 29. Graphically integrating the area under the steam stripping column bottoms line indicated a furfural concentration average of approximately 0.01% by weight. As shown in the Furfural Balance, Table 7, the furfural adsorbed was calculated to be 3.52 lb (1.6 kg). That recovered was 3.74 lb, (1.7 kg) or 106% of that calculated to be adsorbed. Considering the time it was held in the column, furfural is quite stable under the operating conditions to which it was subjected.

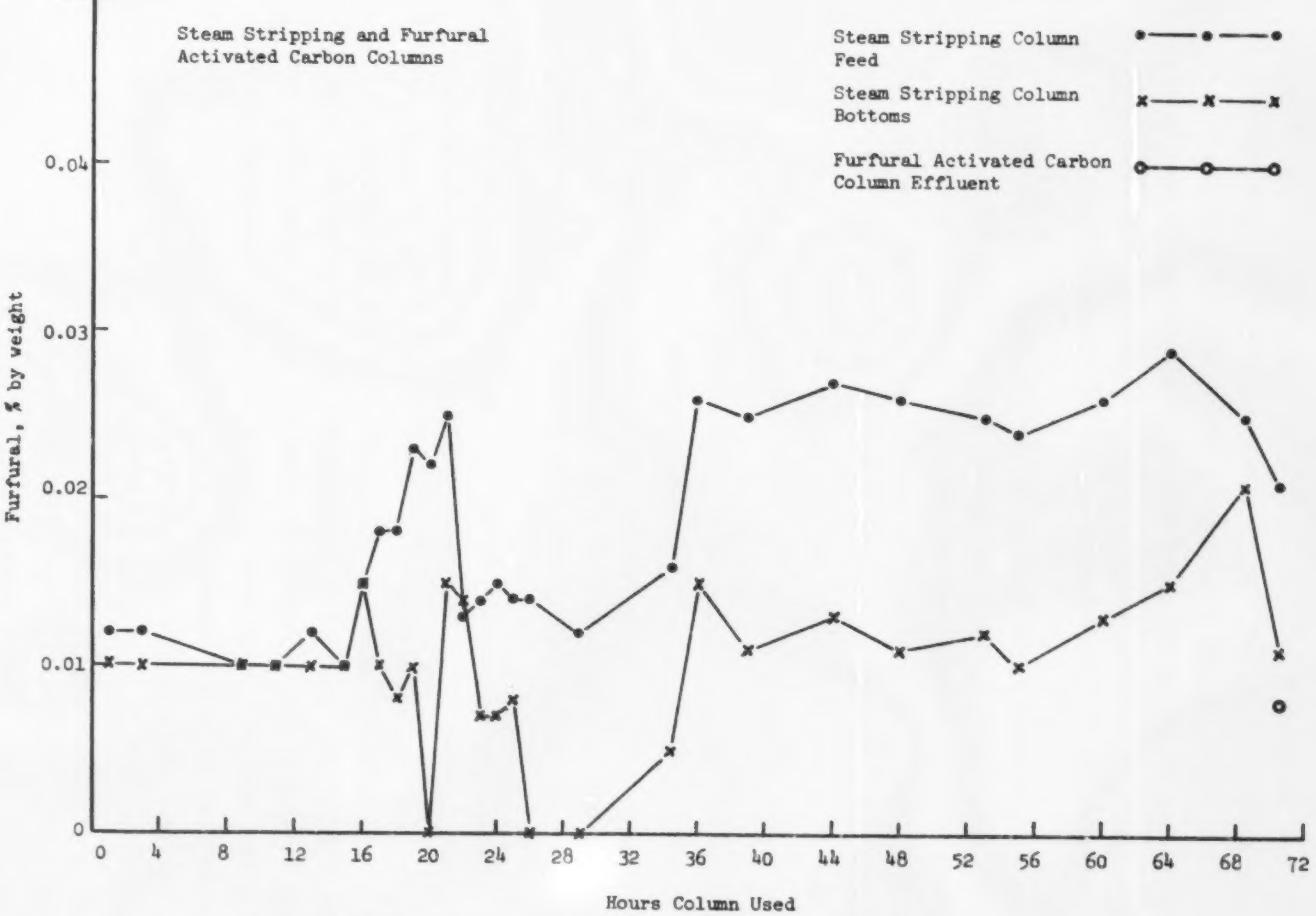


Figure 29. Furfural concentrations – steam stripping and furfural activated carbon column flows

Table 7. FURFURAL BALANCE ACTIVATED CARBON ADSORPTION
10-9-72 to 11-15-72

Furfural adsorbed

Furfural = 1.0 gpm (60 min./hr) (8.33 lb/gal.) (70.5 hr) (0.0001)
= 3.52 lb (1.596 kg)

Furfural recovered — methanol regeneration

Sample No. 359 = 330 g
Analyses = 88.8% furfural
91.0% furfural
Average = 89.9% furfural
Furfural = 330 g (0.899) = 296 g
Sample No. 360 = 435 + 555 + 530 = 1520 g
Analyses = 88.5%
= 91.0%
= 90.5%
= 93.8%
= 93.6%
= 93.4%
= 93.4%
= 92.6%
= 93.1%
= 92.5%
Average = 922.4/10 = 92.2%
Furfural = 1520 (0.922) = 1400 g
Furfural recovered = (296 + 1400)/454 = 3.74 lb (1.697 kg)
% Furfural recovery = (3.74/3.52) 100 = 106%

Activated Carbon Columns-Regeneration

The activated carbon was regenerated as shown in Fig. 3 and 4. That adsorbing primarily acetic acid was regenerated vaporizing ethanol, while that adsorbing furfural was regenerated vaporizing methanol. The Furfural Balance, Table 7 was discussed. The Acetic Acid Balance, Table 8, shows 6.65 lb (3.02 kg) of acetic acid adsorbed in 3 trial runs. This is the equivalent of 9.75 lb (4.42 kg) of ethyl acetate. Since no analytical program was prepared to analyze the wide range of ethyl acetate samples recovered in each run, they were batch distilled, and the overhead samples analyzed for ethyl and methyl acetate concentration. The results were used to calculate the total ethyl acetate recovered. The equivalent of 9.13 lb (4.14 kg) of ethyl acetate, or 93.7% of that retained on the carbon was recovered. Ethyl acetate purity of 89% by weight was accomplished. The remaining 11% was water and ethanol, indicating pure ethyl acetate was possible.

It took approximately 16 and 24 hours operating time to regenerate the carbon adsorbing acetic acid and furfural, respectively. While this presented no problem for that retaining the furfural, it must be reduced for that retaining acetic acid. The limiting factor for regenerating the activated carbon retaining acetic acid is the heat exchanger vaporizing the ethanol. This unit was too small. An optimum vapor rate through the carbon has not been established. The 16-hour period was used to assure maximum conversion of acetic acid to ethyl acetate, maximum ethyl acetate recovery, and maximum ethanol recovery. Since no gas chromatograph was available for pilot plant use, no effort was made to optimize regeneration time.

While efforts were expended to maximize SO_2, methanol, furfural, and acetic acid recovery, as much polymerized material was recovered when regenerating the activated carbon holding furfural as furfural. Polymerized material was also recovered from regenerating the activated carbon containing acetic acid. No efforts were made to determine the quantity. Whereas most of that coming from the furfural carbon was not

Table 8. ACETIC ACID BALANCE ACTIVATED CARBON ADSORPTION
10-9-72 10-23-72 11-6-72

Acetic acid absorbed

10-9-72

By graphic integration — large squares
5 + 8-5/8 + 7-3/4 + 3-1/2 + 4-1/2 + 3-1/2 = 32-7/8 - 11-7/8
= 21

One square = 0.02% by weight per hour
Acetic acid absorbed = 21 (0.0002) (1 gpm) (60 min./hr) (8.33 lb/gal.)
= 2.1 lb (0.954 kg)
Drainage = 60 gallon
Acetic acid in drainage = 60 (8.33) (0.00199)
= 500 (0.00199) = 0.995 lb (0.452 kg)
Total acetic acid absorbed = 2.1 - 1.0 = 1.1 lb (0.50 kg)

10-23-72

By graphic integration — large squares
16.8 + 14.5 + 9.0 + 2.5 = 42.8 squares
Acetic acid absorbed = 42.8 (0.0002) (1) (60) (8.33)
= 4.28 lb (1.942 kg)
Drainage = 60 gallon
Acetic acid in drainage = 60 (8.33) (0.0021)
= 500 (0.0021)
= 1.05 lb (0.476 kg)
Total acetic acid absorbed = 4.28 - 1.05 = 3.23 lb (1.465 kg)

11-6-72

By graphic integration — large squares
12.0 + 12.9 + 9.3 - 1.0 = 33.2
Acetic acid absorbed = 33.2 (0.0002) (1) (60) (8.33)
= 3.32 lb (1.507 kg)
Drainage = 1.0 lb (0.457 kg)
Total acetic acid absorbed = 3.32 - 1.0 = 2.32 lb

Total acetic acid absorbed in 3 runs
Acetic acid = 1.10 + 3.23 + 2.32 = 6.65 lb (3.02 kg)

Total acetic acid absorbed as ethyl acetate
Ethyl acetate = 6.65 (88/60) = 9.75 lb (4.42 kg)

Table 8 (cont'd). ACETIC ACID BALANCE ACTIVATED CARBON ADSORPTION
10-9-72 10-23-72 11-6-72

Total ethyl acetate recovered

Sample No. 349 = 430 g (0.55) = 236 g
No. 350 = 430 g (0.81) = 348 g
No. 351 = 430 g (0.85) = 365 g
Sample broken = 860 g (0.85) = 730 g
No. 352 = 2170 g (0.78) = 1692 g
No. 353 = 910 g (0.55) = 501 g
No. 354 = 570 g (0.17) = 97 g
No. 355 = 385 g (0.01) = 4 g

3973 g

Total ethyl acetate recovered = (3973/454) = 8.75 lb (3.97 kg)
Ethyl acetate in ethanol = 30 gal. (8.33) (0.0005) = 0.12 lb (0.0545 kg)
Methyl acetate = 430 g (0.20) = 86 g
= 430 g (0.03) = 13 g

= 0.22 lb = 99 g
(0.10 kg)

Methyl acetate as ethyl acetate = 0.22 (88/74) = 0.26 lb (0.116 kg)
Ethyl acetate accounted for = 8.75 + 0.12 + 0.26
= 9.13 lb (4.14 kg)

% Accountability = (9.13/9.75) 100 = 93.7%

volatile, that coming from the acetic acid carbon was. However, it polymerized or reacted during the processing in the fractionation column and lost its volatility. The nonvolatile material from both columns are to be recycled back to the concentrated evaporator liquor for burning or spray drying purposes. In the pilot plant this material was discharged to the drain with the water at the bottom of the fractionator at 15% by weight solids concentration. No attempt was made to increase this solids concentration.

Evaporator Studies

Throughout the period that the multipoint temperature recorder was being repaired and the pilot plant was sitting idle, arrangements were made to discuss in detail Consolidated's evaporation system with their supervisors and engineers. After these discussions it was agreed that it would be beneficial to analyze the evaporator condensates from each effect of their Rosenblad evaporator system. With Consolidated Papers Inc.'s permission the results of these analyses are included as part of this report. They are expressed as % by weight as follows:

	Methanol	Acetic Acid	Furfural
Weak spent liquor feed	0.090	0.410	0.045
Condensate from 50% solids effect	0.005	0.463	0.005
35% Solids effect	0.010	0.421	0.010
20% Solids effect	0.006	0.210	0.005
10% Solids effect	0.071	0.314	0.021

The condensate accumulated from one effect to another, but not necessarily directly from the 50% solids effect through the 35% and 20% effects to the 10% effect. No detail about the path of the condensate will be given, since time will not permit an adequate description of it. Consolidated has switching procedures that are too complicated to describe without drawings. The important factor was that the condensate from the 10% solids effect includes the condensate from all other effects. Therefore, it is apparent that the bulk of the methanol and furfural were removed in the 10% solids effect. Note that, although condensate flow is less than weak spent liquor feed flow, the condensate had 79% of the methanol concentration, 77% of the acetic acid concentration, and 47% of the furfural concentration that was in the feed. This indicated an appreciable loss of those chemicals in the evaporation system. If equal evaporation is assumed in each evaporator effect, it is apparent that almost 4 times the methanol and furfural concentration, or a 0.28% methanol and 0.084% furfural, would occur in the condensate from the 10% solids effect if the other condensates were separated. Examination of Fig. 9 shows that the other 75% of the evaporator condensate contains substantially less methanol than our best steam stripped evaporator condensate. Essentially the same thing is true for the furfural (see Fig. 29).

Project Status in February, 1973

The merits of these unit operations have been established. A high percentage of SO_2 vapor that can be reused in the mill has been produced. Crude methanol, furfural, and ethyl acetates have been recovered. Four important areas of study must be further developed before this process is ready conclusively for commercialization:

1. A market for the crude products produced must be established.
2. The life of the carbon must be determined when feeding evaporator condensate that has been used as a backwash in the evaporators.
3. Regeneration procedures for the activated carbon used in adsorbing acetic acid must be optimized.
4. An overall economic evaluation of the process is required.

To date the evaporator condensate used was readily available from the Consolidated Papers, Inc.'s mill without suggesting any changes in their operating procedures for producing and/or utilizing their evaporator condensates. The condensate feed was less than ideal for their purpose. Since they have several evaporator systems, a composite of their condensates was processed after these flows had been used for evaporator wash. The feed is dilute and contains lignosulfonates and other spent liquor solids. The chemical concentrations expressed as % by weight varied as follows:

	High	Low	Mean	
Methanol	0.170	0.025	0.065	
Acetic Acid	0.364	0.170	0.268	
Furfural	0.040	0.010	0.016	
Sulfur Dioxide-TI	0.233	0.017	0.064	
Sulfur Dioxide-OLC	0.076	0.015	0.034	
Biochemical Oxygen Demand	6540	2270	4063	milligrams per liter

The methanol, furfural, and acetic acid balances, Tables 5, 6, 7, and 8, were made using the instantaneous values, graphically integrating to determine recoverable quantities. The main function of these balances was to determine operating and analytical proficiency. The evaporator studies had already indicated that splitting the evaporators and/or their condensates was the path to pursue for Consolidated Papers, Inc.'s Appleton Mill. No other mill showed any enthusiasm for this approach.

Since the establishment of a market for the crude products was essential to the economic evaluation of the process, the following information was presented. Assuming 300,000 gallons (1,134,000 liters) per day evaporator condensate capacity for the Consolidated Mill and using the mean concentrations list in the "Previous Work" section and 350 days operation per year, Consolidated Papers, Inc. produced the following:

Methanol	569,000 lb/year	258,500 kg/year
Acetic acid	2,345,000 lb/year	1,063,000 kg/year
Furfural	140,000 lb/year	63,600 kg/year

Sulfur dioxide (TI)	560,000 lb/year	254,500 kg/year
Sulfur dioxide (OLC)	298,000 lb/year	135,300 kg/year

Conversion of the acetic acid to ethyl acetate would give 3,440,000 lb/year (1,560,000 kg/year).

The product value is:

Ethyl Acetate

Market value — 3,440,000 ($0.12) = $412,000
Mill value — 3,440,000 ($0.09) = $310,000

Furfural

Market value — 140,000 ($0.175) = $ 24,500
Mill value — 140,000 ($0.138) = $ 19,300

Methyl Alcohol

Market value — (569,000/7.5) ($0.12) = $ 9,100
Mill value — (569,000/7.5) ($0.104) = $ 7,900

Sulfur Dioxide

Market value — (858,000/2) ($0.001) = $ 4,290
Mill value — (858,000/2) ($0.001) = $ 4,290

Total Market Value = $412,000 + $24,500 + $9,100 + $4,290 = $449,890

Total Mill Value = $310,000 + $19,300 + $7,900 + $4,290 = $341,490

Cost of Ethanol = $166,000

Money left to pay for operating costs, capital expenditure, maintenance, etc. = $175,490

No credit was taken for reusable water and/or elimination of pollution problems. It was believed that the capital costs will compare favorably with the secondary treating process for this waste flow.

A more complete analysis of this same information based on actual complete material and heat balances on the pilot system are presented in a later section.

Process Options

The following process options were presented at a meeting of the cooperators on January 17, 1973 and remain as valid options for application of the system.

1. Separate the evaporator condensates from the various effects, so that only that portion high in methanol, furfural, and sulfur dioxide is steam stripped, and those high in acetic acid are adsorbed on the activated carbon.
2. Steam strip the weak spent liquor to remove SO_2, methanol, and furfural before the evaporators. Recycle the portion of condensate weak in acetic acid concentration, and send that which is more concentrated to the activated carbon adsorbers.
3. Adsorb the furfural directly from the weak spent liquor with activated carbon before evaporation. Separate the evaporator condensates, so that only that portion with concentrations high in methanol and sulfur dioxide is steam stripped, and those with concentrations high in acetic acid are adsorbed on the activated carbon.
4. Steam strip that portion of the evaporator condensate with concentrations high in methanol, furfural, and sulfur dioxide. Neutralize the overhead with $Ca(OH)_2$ to destroy the furfural and sulfur dioxide. Recover the methanol in the fractionation column. Adsorb those portions of evaporator condensate high in acetic acid concentration on activated carbon. Regenerate the carbon with methanol. Treat the regeneration effluent with $Ca(OH)_2$ to destroy the furfural and methyl acetate. Recycle and recover the methanol in the fractionator. Spray dry the $Ca(OH)_2$ reaction products.
5. Adsorb furfural and acetic acid in one activated carbon column, regenerate the carbon with ethanol, recover the ethyl acetate, furfural, and ethanol.
6. Recycle the ethyl acetate-ethanol regenerating agent until the ethyl acetate concentration is at its economical peak. Recover

chemicals at a central location. Over 8 1/2% by weight ethyl acetate in ethanol was used in the pilot studies at Scott with no adverse effects in carbon regeneration.

7. Design and do economic evaluation on the process as it is now operated. Use the best available data.
8. Identify and evaluate the acids and other chemicals removed with the furfural.
9. Rerun equipment as it is now installed to establish carbon life.

Additional Experimental Operation and Evaluation of Pilot System

Methodology

During the January 17, 1973 meeting of the members of this Group Project it was agreed that Mr. Lueck continue with his low temperature, thermal, activated carbon regeneration work, while Mr. Baierl pursue Process Options 5 and 9 of the nine options presented. Unfortunately, it was not possible to run these experiments simultaneously. Initial emphasis was placed on Mr. Lueck's work. The pilot plant was modified to provide processed evaporator condensate to his unit as shown on Fig. 30. Recirculation pumps were added at the bottom of the steam stripping and fractionation columns, and water lines were eliminated. Simultaneously, the steam stripping column condensed overheads were fed into the fractionation column in an effort to optimize its size and operation, and studies were made on Consolidated Papers Aqua Chem No. 1 and Rosenblad evaporation units.

Evaporator Studies

The data in Table 9 were compiled during the evaporator studies, while the Aqua Chem No. 1 units were operated in series with and ahead of the Rosenblad units.

It was readily discernible from these data that it would be advantageous for Consolidated Papers, Inc. to separate these condensates. The condensate flow was from Effect 3 to Effect 2 to Effect 1 to Effect 4

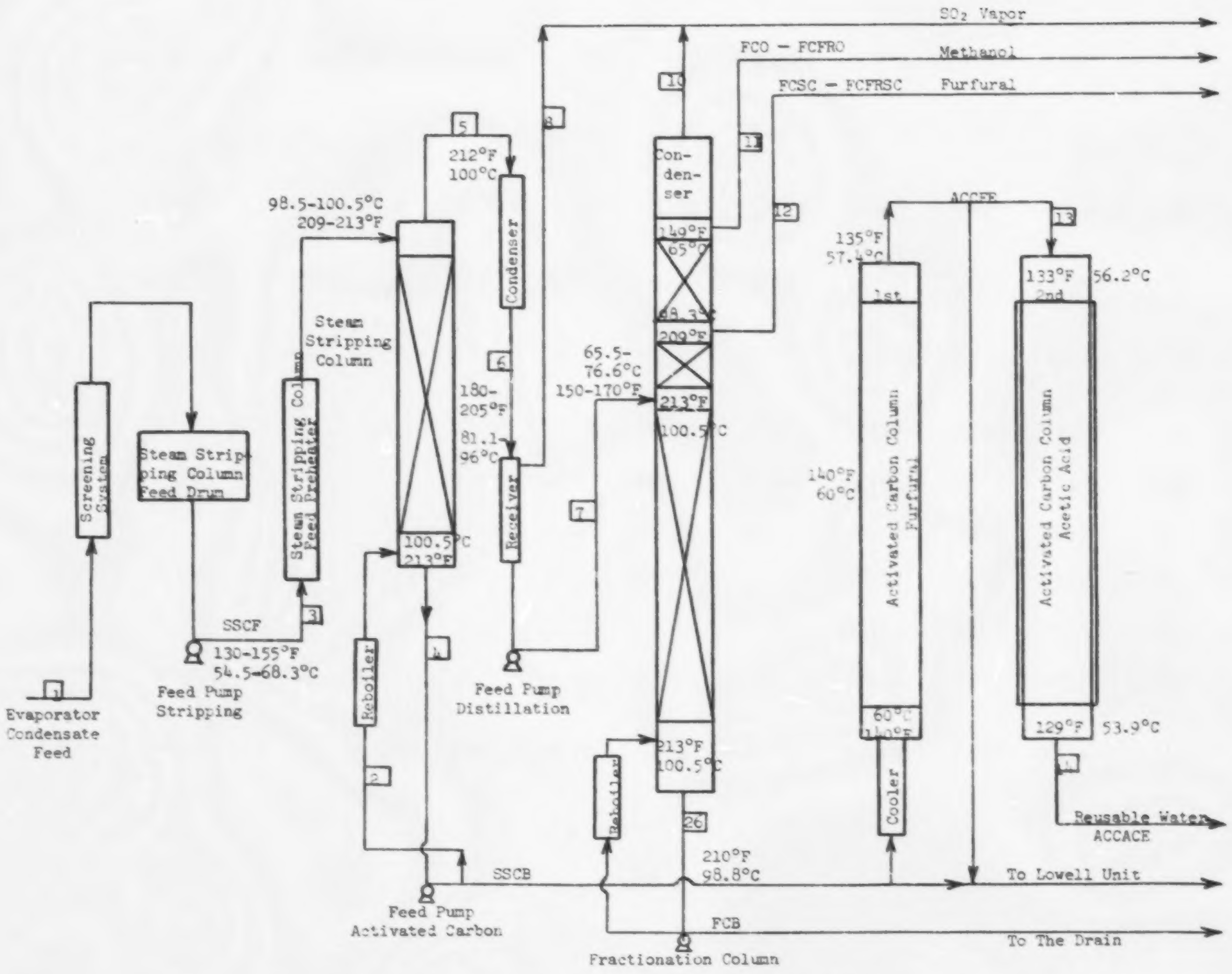

SO₂ Vapor
Methanol
Furfural
FCO – FCFRO
FCSC – FCFRSC
10
11
12
13
5
8
6
7
3
2
4
1
26
Con-
den-
ser
149°F
65°C
68.3°C
209°F
213°F
100.5°C
213°F
100.5°C
212°F
100°C
98.5-100.5°C
209-213°F
Steam
Stripping
Column
Condenser
180-
205°F
81.1-
96°C
65.5-
76.6°C
150-170°F
Screening
System
Steam Stripping Column Feed Drum
Steam Stripping Column Feed Preheater
100.5°C
213°F
Receiver
SSCF
130-155°F
54.5-68.3°C
Evaporator
Condensate
Feed
Feed Pump
Stripping
Reboiler
Feed Pump
Distillation
Reboiler
Feed Pump
Activated Carbon
SSCB
210°F
98.8°C
FCB
Fractionation Column
ACCFE
135°F
57.4°C
1st
Activated Carbon Column
Furfural
140°F
60°C
60°C
140°F
Cooler
133°F
2nd
56.2°C
Activated Carbon Column
Acetic Acid
129°F
53.9°C
Reusable Water
ACCACE
To Lowell Unit
To The Drain

Figure 30. Modified IPC pilot plant – Consolidated Papers, Inc. Appleton mill

Table 9. EVAPORATOR STUDIES DATA

1. Operation on Channel A

Sample	% by Weight			pH	% Solids		SO_2, g/l		VOA, mg/l			BOD_5, mg/l
	MeOH	HAc	Furf.		Neut.	24 Hr	TI	OLC	Total	HAc	Formic	
Aqua Chem Feed	0.069	0.340	0.028	2.85	10.34	9.90	0.804	3.996	4212	4177	27	
Aqua Chem Prod. Rosenblad Feed	0.035	0.343	0.023	3.70	12.87	12.60	0.252	3.975	3792	3583	160	
Rosenblad #3	0.018	0.330	0.023	3.89	15.16	14.71	0.183	4.179	3901	3717	141	
Rosenblad #4	0.01	0.386	0.020	4.05	20.58	20.39	0.207	5.421	4602	4100	385	
Rosenblad #1				4.03	31.82	32.19	0.411	6.054	6340	5691	498	
Rosenblad #2				4.05	54.73	55.57	0.604	9.171	6736	5295	1105	
Aqua Chem Cond.	0.113	0.210 0.240	0.03	2.89	0.29	0.07	0.040	0.048	1969	1948	16	3357
Aqua Chem Scrubber Cond.	0.205	0.219	0.06	2.52	0.27	0.03	0.084	0.147	2006	2006	0	4241
Rosenblad #3 Cond.	0	0.431	0	2.61	0.57	0.12	0.037	0.253	4054	4054	0	3798
Rosenblad #2 Cond.	Trace	0.373	0	2.55	0.50	0.09	0.131	0.227	3590	3577	10	2892
Rosenblad #1 Cond.	0	0.255	0	2.88	0.30	0.06	0.024	0.103	2201	2193	6	1618
Rosenblad #4 Cond.	0.02	0.252	0.12	2.21	0.48	0.14	0.796	0.267	2871	2860	8	2409

Table 9 (cont'd). EVAPORATOR STUDIES DATA

2. Operation on Channel B

	% by Weight				% Solids		SO_2, g/l		VOA, mg/l			BOD_5,
Sample	Meth.	HAc	Furf.	pH	Neut.	24 Hr	TI	OLC	Total	HAc	Formic	mg/l
Aqua Chem Feed	0.066 0.054	0.336 0.321	0.032 0.029	2.83	11.88	11.53	0.507	4.588	4359	4330	22	
Aqua Chem Prod. Rosenblad Feed	0.028	0.337	0.016	3.59	14.55	14.44	0.181	4.182	3962	3900	48	
Rosenblad #3	0.010	0.328	0.015	3.85	16.86	16.95	0.157	4.305	3962	3886	58	
Rosenblad #4	Trace	0.311	0.016	3.88	22.09	23.03	0.206	5.920	4633	4552	62	
Rosenblad #1				3.98	31.85	34.53	0.281	7.020	6096	6031	50	
Rosenblad #2				4.45	53.27	54.69	0.583	11.162	7254	7150	80	
Aqua Chem Cond.	0.108	0.273	0.023	3.01	1.15	0.91	0.053	0.375	2390	2377	10	
Aqua Chem Scrubber Cond.	0.132	0.242	0.028	2.64	0.37	0.09	0.056	0.142	2512	2496	12	
Rosenblad #3 Cond.	0	3.387	0	2.48	0.59	0.10	0.054	0.140	4151	4138	10	
Rosenblad #2 Cond.	0.01	0.380	0	2.50	0.51	0.04	0.080	0.094	3718	3705	12	
Rosenblad #1 Cond.	0	0.293	0	2.80	0.31	0.03	0.013	0.111	2384	2371	10	
Rosenblad #4 Cond.	0.021	0.284	0	2.25	0.42	0.07	0.452	0.262	2786	2773	10	

cumulatively. Steam was added to that in Effect 1. Consequently, considerable methanol and furfural were added in Effect 4 to bring the cumulative condensate to their final concentrations. To verify this, samples of the condensates made in Effect 4 only were analyzed, with the following results:

Sample	% by Weight				SO_2, g/l	
	MeOH	HAc	Furf.	EtOH	TI	OLC
Channel A — 2:30 p.m.	0.18	0.23	0.05	0.01	1.39	0.48
Channel A — 3:30 p.m.	0.19	0.23	0.06	0.01	1.51	0.54
Channel B — 2:30 p.m.	0.20	0.28	0.08	0	--	--
Channel B — 3:30 p.m.	0.26	0.26	0.06	0	--	--

Prior composite condensates showed methanol and furfural to be in the 0.04 to 0.05 and 0.01 to 0.02 concentration ranges, respectively. Almost 4 times the methanol and furfural concentrations had been conservatively predicted.

Since all condensates from Effects 3, 2, and 1 had less methanol and furfural in them than the majority of the steam stripping column bottoms, they should be kept separate and out of the steam stripping column system. Thus, the equipment size in both the steam stripping and fractionation systems will be substantially lowered, as will the steam requirement.

The data in Tables 10, 11, and 12 were submitted by one of the cooperators and are compared with data from Scott (Table 21) and from Consolidated (Table 22).

First note the ineffective steam stripping at Scott. This was the initial work in 1969. Sixteen ft (487.7 cm) of packing and 10% steam were used. Now look at Consolidated in April, 1973 using 4 ft (121.9 cm) of packing and 6% steam. This re-emphasizes what over-design can do. No problems with scaling or plugging were encountered in this column, either at Scott or Consolidated, after the screening system was installed. The figures from the cooperator were sent to demonstrate little differences in acetic acid concentration in their

Table 10. ANALYSES OF EVAPORATOR EFFECTS OF COOPERATOR MILL

	Solids content wt. %	Volatile acids on solids as acetic acid, wt. %	Calculated volatile acids in condensate as acetic acid, wt. %
Feed	13.2	10.6	1.54
From 5th	17.66	9.2	1.83
4th	21.88	7.2	0.945
3rd	31.24	5.9	2.19
2nd	55.51	2.6	--

Table 11. CARBON ADSORPTION WORK AT SCOTT PAPER COMPANY
OCONTO FALLS EVAPORATOR CONDENSATE

	As received	Steam stripped
Methanol	0.119% by weight	0.049% by weight
Acetic acid	0.600% by weight	0.530% by weight
Furfural	0.122% by weight	0.048% by weight

Steam stripping column — 4-inches deep x 16 feet high using 10% by weight of feed stripping steam.

Table 12. CARBON ADSORPTION WORK AT CONSOLIDATED PAPERS, INC.
APPLETON DIV. EVAPORATOR CONDENSATE

	As received mean	April 23, 1973 — 11:30 AM	
		As received	Steam stripped
Methanol	0.065% by weight	0.06% by weight	0.01% by weight
Acetic acid	0.268% by weight	0.21% by weight	0.22% by weight
Furfural	0.016% by weight	0.01% by weight	0.00% by weight

Steam stripping column — 4 feet deep x 4 feet high using 6% by weight feed stripping steam.

evaporator effects. There is a dual purpose for showing them. First the number of hours the activated carbon adsorbed acetic acid was almost identical for these condensates. The carbon load at Scott was 10%, and 3 to 4% at Consolidated. That is about 20 times the concentration. That means the carbon loading for this condensate showing 1.54 to 2.19% by weight would be 30 to 40%. The second fact that this could be 40% versus 30% shows the increase in concentration is significant for the developed process. Furfural has a multiple of over 100. The loading at Consolidated was 1 to 2% from 0.01 to 0.02% concentration. At Scott it was 20 to 30% for a 0.2 to 0.3% concentration.

Fractionation

As the steam stripping system and activated carbon column-furfural were providing feed to the Lowell Unit, the fractionation column system was run to establish optimum equipment size. On February 1, 1973 evaporator condensate was pumped through the steam stripping column preheater to the fractionation column at a point about 14 feet above the bottom of the column. The rate was 0.76 gpm (2.88 l/min.).

From the following data it was apparent that the fractionation column rapidly lost its efficiency:

		% by Weight		
Sample	Time	MeOH	HAc	Furfural
Feed	11:35 a.m.	0.030	0.240	0.012
Bottoms	11:35 a.m.	0.010	0.260	0
Feed	3:30 p.m.	0.055	0.215	0.010
Bottoms	3:30 p.m.	0.030	0.210	0.007

Column flooding occurred about 4 feet below the feed. The following data showed a similar run in the 4-foot steam stripping column, with equivalent steam to that used in the fraction column:

Sample	Time	% by Weight MeOH	 HAc	 Furfural
Feed	1:40 p.m.	0.045	0.216	0.013
Bottoms	1:40 p.m.	0.005	0.189	0

This pointed out the disadvantages of overdesign; it can be worse than underdesign. These results verified similar work at Scott Paper Company's Everett Mill.

From February 12 through February 22, 1973 the evaporator condensate was pumped through the steam stripping column system at the rate of 0.5 gpm (1.9 l/min.). Approximately 10% by weight of feed stripping steam was used, and the condensed overhead was processed in the fractionation column system. The stripping column bottom liquid was either processed through the activated carbon column and/or drained. The main objectives were to determine the capacity of the fractionation column system, to establish carbon loading times and to provide loaded activated carbon units for further regeneration work. Using a 1 to 1 ratio of feed to steam in the fractionation column, furfural was removed as a 90%+ by weight crude from the bottom splitter, while no methanol or furfural was detected in the fractionation column bottom liquor. This indicated that only 9 ft (274 cm) of Goodloe Packing was necessary to remove all the furfural in the steam stripping column condensed overhead vapors. The 9 ft (274 cm) of packing was probably conservative, since the fractionation column feed was introduced in the column above the furfural take-off point. It was interesting to note that the furfural coming off the middle splitter, above the feed, had about 1.0% by weight methanol in it, whereas that coming off the bottom splitter, under the feed, showed little or no methanol in it. Approximately 1565 g, or 3.5 pounds of 90%+ by weight methanol was held in the top of the fractionation column.

Activated Carbon Adsorption and Regeneration

Since the activated carbon column-acetic acid was loaded and the activated carbon column-furfural was partially loaded, it was decided to regenerate them in series with ethanol in accordance with Process Option 5. The regeneration proceeded as shown in Fig. 31. Ethanol, at the rate of 1 gpm, (3.8 l/min.) was pumped into the top of the activated carbon column containing essentially acetic acid for 12 minutes. By plug flow essentially 10 gallons (37.8 l) of water containing less methanol and acetic acid than in the evaporator condensate feed was sent to the drain. In a commercial installation this liquid would be pumped to the activated carbon column in parallel with this one for acetic acid adsorption. The steam valve feeding steam to the column jacket was cracked open and that feeding steam to the vaporizer was opened to control the steam pressure to the vaporizer at about 20 psig (1.40 kg/cm^2 gage). Pressure in both columns built up to about 14 psig (0.98 kg/cm^2 gage). Liquid was forced out the activated carbon column containing the furfural through the condenser to the receiver. From there it was pumped at the rate of 0.3 gpm (1.14 l/min.) to the fractionation column, which was partially filled with ethanol. Initially, everything looked great. The liquid to the receiver rapidly discolored. The temperature at the top of the fractionation column was quickly dropping its 173°F (78.3°C) temperature. What appeared to be furfural was collecting in the tap-off section on the bottom splitter of the fractionation column. No furfural was detected in the liquid from the bottom of the fractionation column. By 11:00 a.m. the temperature at the top of the fractionation column had reached 158°F (70.0°C), indicating a good grade ethyl acetate. Since alcohol was building up in the system, a recirculation stream from the middle splitter back to the ethanol feed drum was started. When what appeared to be furfural was removed from the bottom splitter and tested, it was not furfural but highly colored water which had displaced the alcohol. Then the problems arose. To maintain 0.3 gpm (1.14 l/min.) recirculation rate of alcohol, it was necessary to recirculate from the bottom splitter. To avoid carrying water and furfural back to the ethanol feed drum, another receiver was hooked up in parallel with it. This corrected one problem but created another. Furfural and polymerized material was being carried into the activated carbon column that had

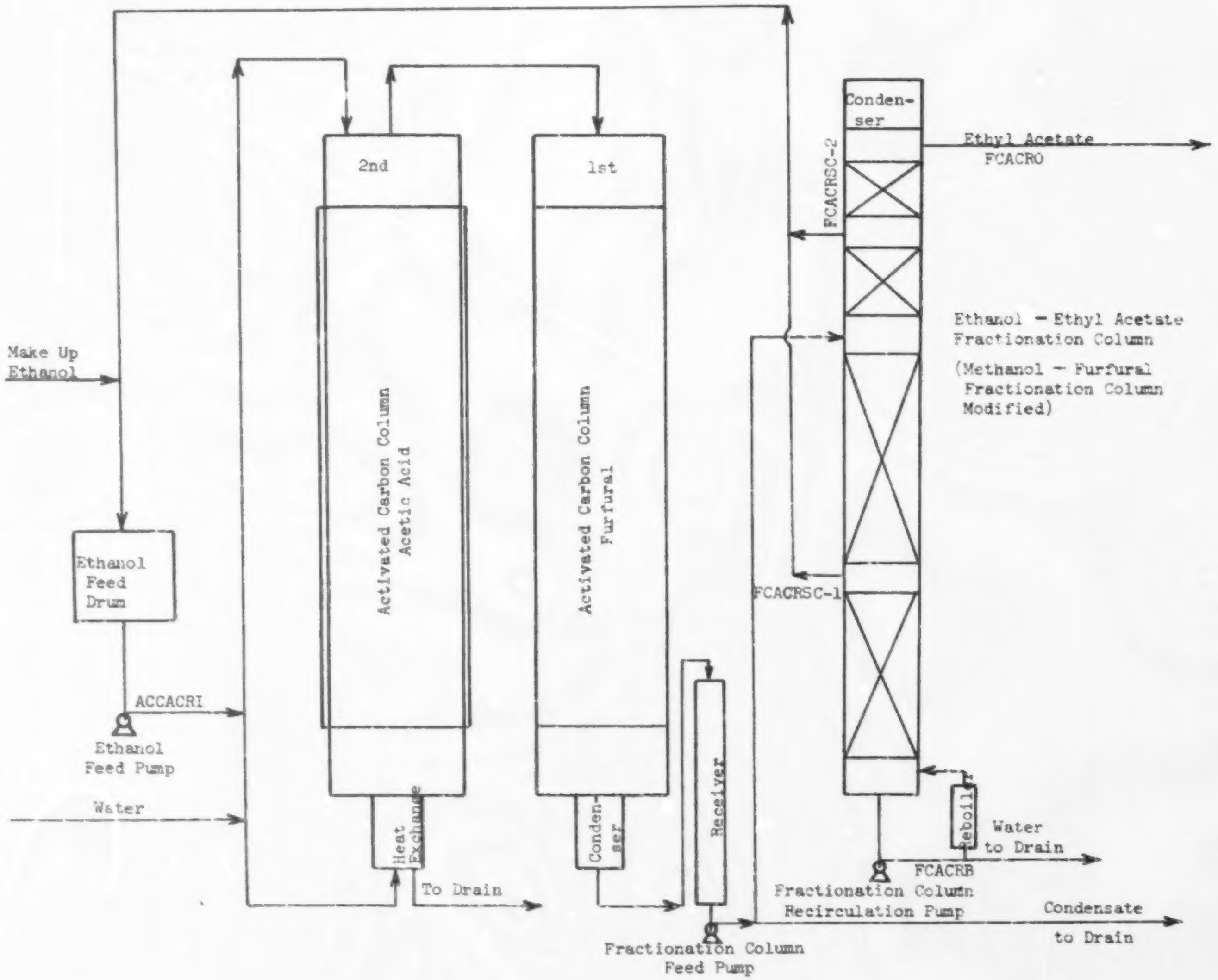

Make Up Ethanol
Ethanol Feed Drum
ACCACRI
Ethanol Feed Pump
Water
2nd
Activated Carbon Column Acetic Acid
Heat Exchange
To Drain
1st
Activated Carbon Column Furfural
Conden-ser
Receiver
Fractionation Column Feed Pump
FCACRSC-2
FCACRSC-1
Conden-ser
Ethyl Acetate FCACRO
Ethanol – Ethyl Acetate Fractionation Column
(Methanol – Furfural Fractionation Column Modified)
Reboiler
Water to Drain
FCACRB
Fractionation Column Recirculation Pump
Condensate to Drain

Figure 31. Both activated carbon columns regenerated with ethanol

previously contained only methanol and acetic acid. By now it was apparent that ethyl acetate, ethanol, furfural, and water removal in one fractionation column was going to be too complicated, so the recovery of furfural was abandoned. It was allowed to go out the bottom of the fractionation column with the water and residual spent liquor solids. The ethanol feed and the steam to the activated carbon column system was shut off. The fractionation column was held at total reflux overnight.

The next day there were two partially regenerated activated carbon columns, about 40 gallons (151.5 l) of ethanol in the complete regeneration system and flow rate limits to the fractionation column of about 0.15 gpm (0.57 l/min.). The regeneration was continued, and the flow rates to the carbon columns were varied from 0.1 (0.38) to 0.3 (1.14 l/min.) gpm. The ethyl acetate was allowed to accumulate in the fractionation column. Although not practical, this system worked well and the carbon columns were regenerated, see Fig. 32. Unfortunately, about mid-morning the water pressure in the main header dropped substantially, and no cooling water reached the condenser at the top of the fractionation column. Over a 15-minute period all the ethyl acetate and ethanol remaining in the top of the column vaporized and discharged through the vent. Even so, the recovery of ethyl acetate was the highest of any run. Although the level in the ethanol storage tank showed almost full recovery of ethanol, results of analyses (two days later) showed water and ethyl acetate in the alcohol and ethanol in the activated carbon column effluent.

Since Process Option 9 was the second choice, it was decided to run the adsorption and regeneration cycles on the two columns in series. Evaporator condensate feed rate was held at 0.5 gpm (1.9 l/min.) and 10% by weight of feed stripping steam was used to assure maximum removal of methanol and furfural. For regeneration, a line was built from the ethanol feed pump to the top of the activated carbon column-furfural, and from the top splitter on the fractionation column to the ethanol feed drum. Water and residual spent liquor was to be removed from the

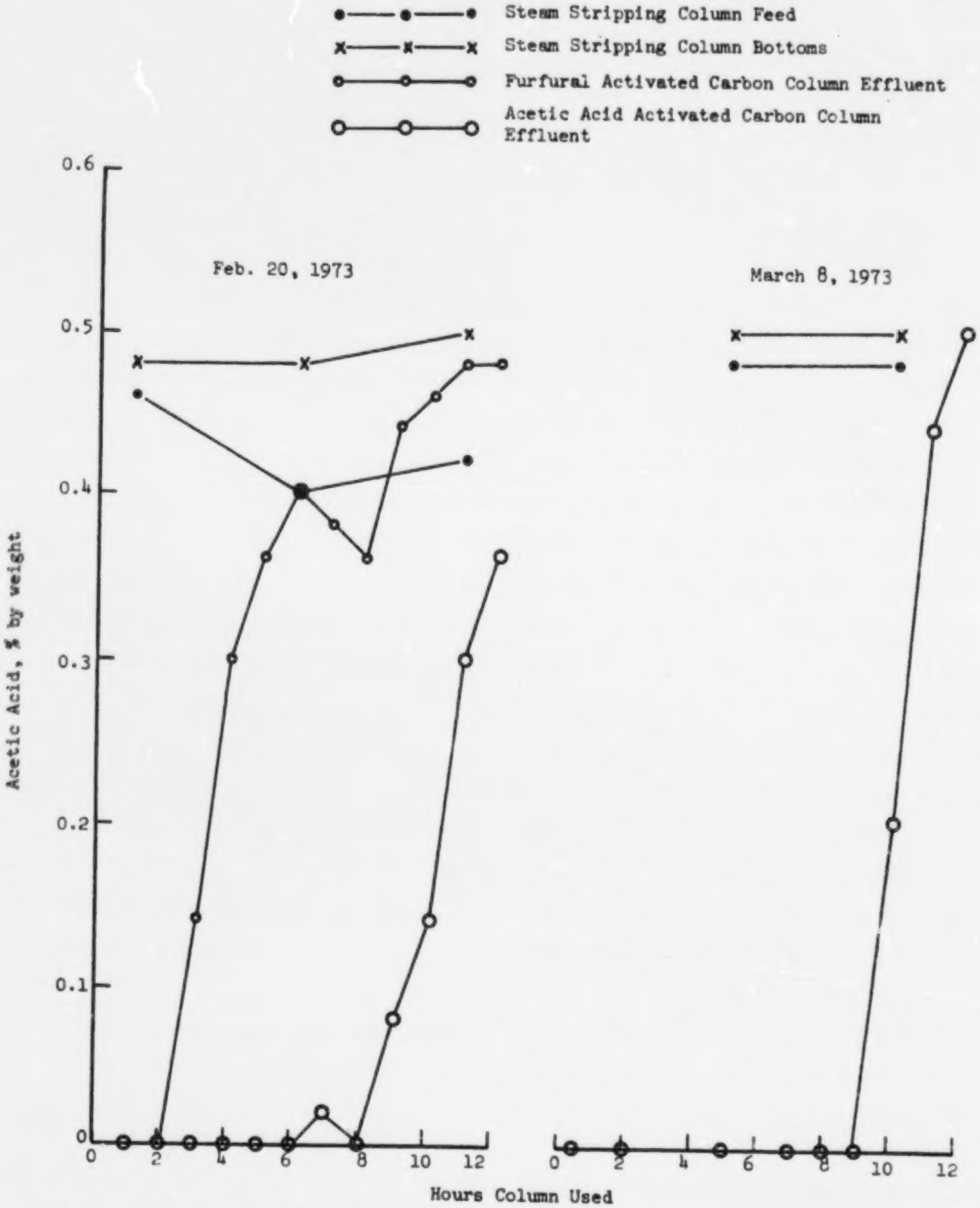


Figure 32. Steam stripping, furfural activated carbon and acetic acid activated carbon columns

bottom of the fractionation column and ethyl acetate would be allowed to build up in the alcohol. Three successive adsorption runs, March 8, 13, and 26, showed the acetic acid coming through progressively earlier; 10 hours, 8 hours, and 7 hours, respectively, see Fig. 32 and 33. However, complete acetic acid loading was still extended beyond ten hours. The real problem became apparent when traces of ethanol appeared in the effluent from the activated carbon column containing acetic acid after it was 7 hours on the adsorption cycle. Black material appeared in the initial condensate effluent. It became apparent that residual spent liquor in the activated carbon column containing acetic acid was not being removed, and that the ethanol was not being quickly removed from the carbon in the activated carbon column containing furfural. Also the ratio of ethanol to water was not high enough. Too much acetic acid was being removed as acetic acid and too much ethanol [almost 40 (151.5 l) gal.] was held in the system. Piping modifications and regeneration system changes for recovery of acetic acid as ethyl acetate and the removal of water and residual spent liquor simultaneously were mandatory.

Four things were learned from these runs:

1. Ethyl acetate, ethanol, furfural, and water were not going to be recovered in one fractionation column.
2. Acetic acid and furfural were effectively removed from both carbon columns.
3. Channeling occurred when going downstream in the Act. Carb. Col. — Fur. and the water and steam with the ethanol made the ethanol recovery expensive.
4. Most importantly the carbon life was deteriorating, due to processing dirty condensates, especially in the Act. Carb. — Acetic acid column.

New Activated Carbon Regeneration System

It was decided to move the heat exchanger from directly under the activated carbon column-acetic acid to a position on the side of the

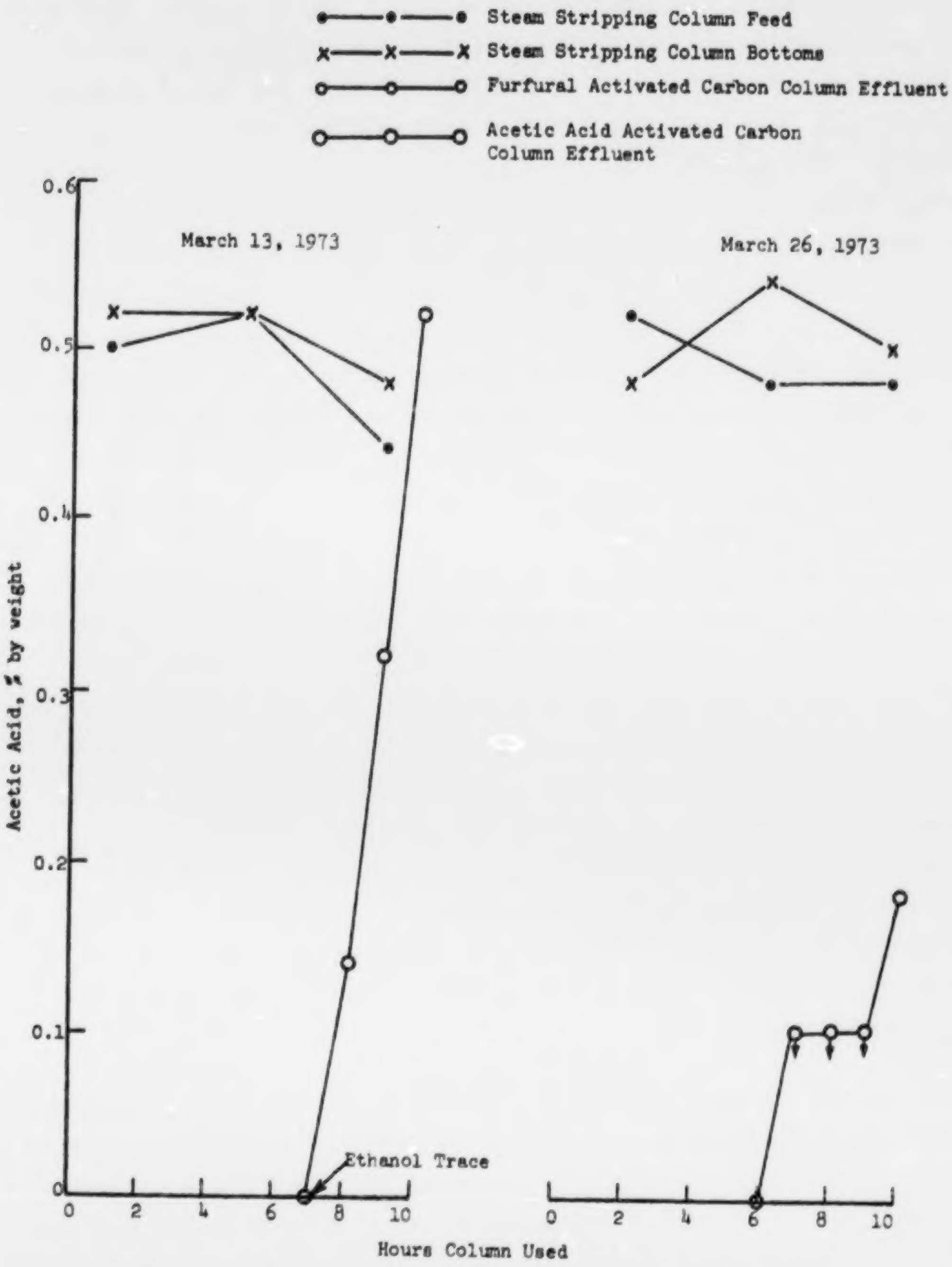


Figure 33. Steam stripping, furfural activated carbon and acetic acid activated carbon columns

column. The vapors would then enter the bottom disengaging section from the side similar to the reboiler on the fractionation column. When this heat exchanger was removed and inspected, better than 60% of its tubes (mostly those around its outer circumference) were completely plugged with the black polymerized material. This verified that there was no escape path for the nonvolatile material and indicated the heat exchanger was too large for the job it was doing. The smaller heat exchanger that was used for vaporizing the methanol when regenerating the activated carbon column-furfural was used to replace this one. Piping modifications and changes to the activated carbon column-acetic acid regeneration system were made in an effort to recirculate liquid through the smaller heat exchanger now installed on the side of the column's bottom disengaging section. Existing equipment, with the exception of new brass pressure gages to replace the older corroded ones, was used. A check of the new system operation, shown schematically in Fig. 34 to 37, indicated that theoretically it functioned well. However, so much black material, plastic in appearance, was removed it plugged the rotometer, pumps, and packing in the fractionation column. Operational problems, such as controlling the steam pressures and feed rates, were encountered. Steam pressure regulators had to be changed, and since all but one pump that was available lost their flows when discharge pressures exceeded 15 psig (1.05 kg/cm^2 gage), maintaining constant flows was almost impossible. With erratic operation, it was extremely difficult to know what the concentrations of ethyl acetate, ethanol, and water were in the various streams. Attempts were made to get a gas chromatograph capable of determining these in extreme concentrations. None was available.

During the latter part of March and the early part of April a concentrated effort was made to perfect the new regeneration system. Ethanol-water runs were made to establish steam pressure controls and constant pumping rates. In previous regeneration experiments no reflux was used in the activated carbon column. The new system is demonstrated in Fig. 34 through 37. In this system steam rates had been reduced to the

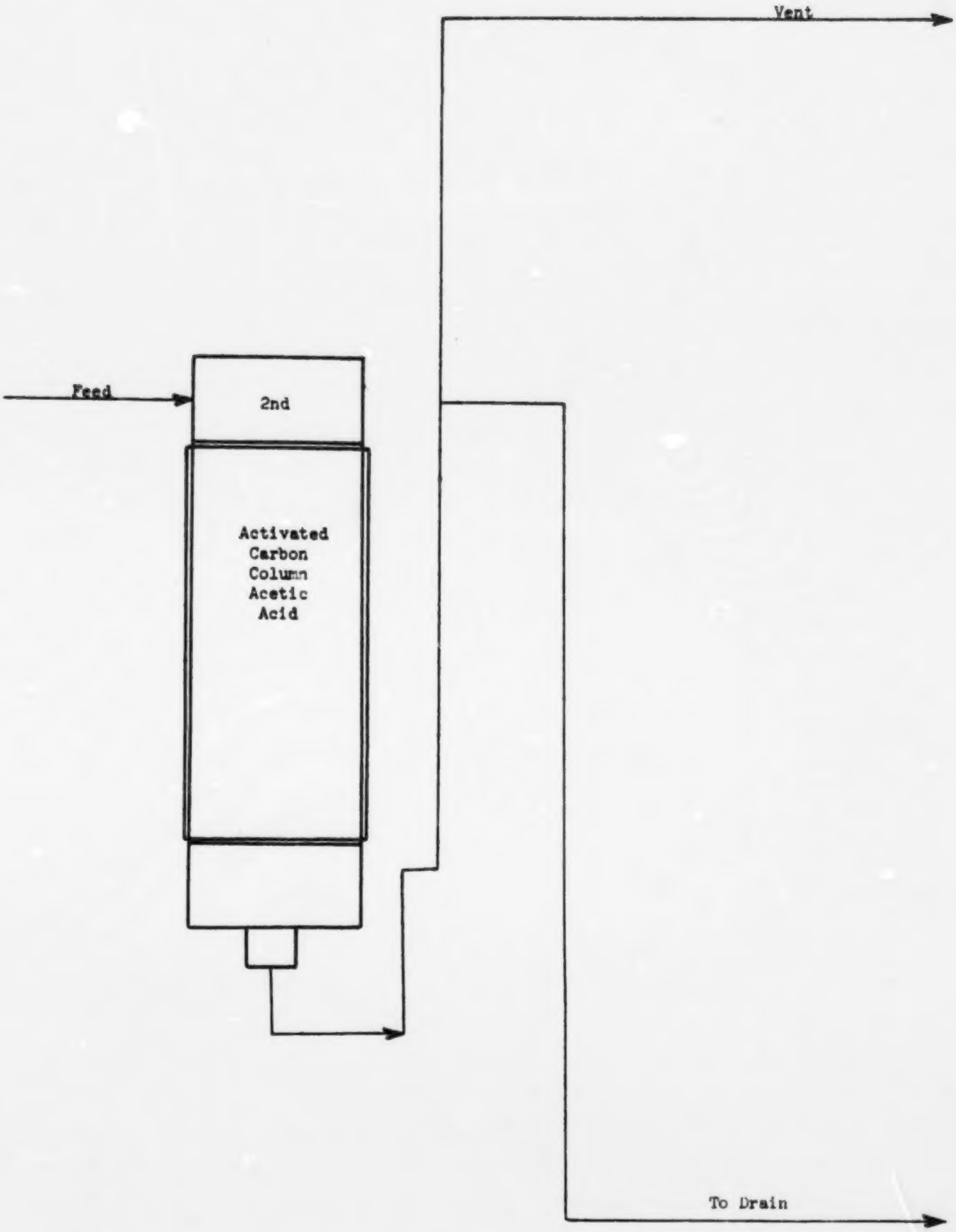

Vent
Feed
2nd
Activated
Carbon
Column
Acetic
Acid
To Drain

Figure 34. Process flow

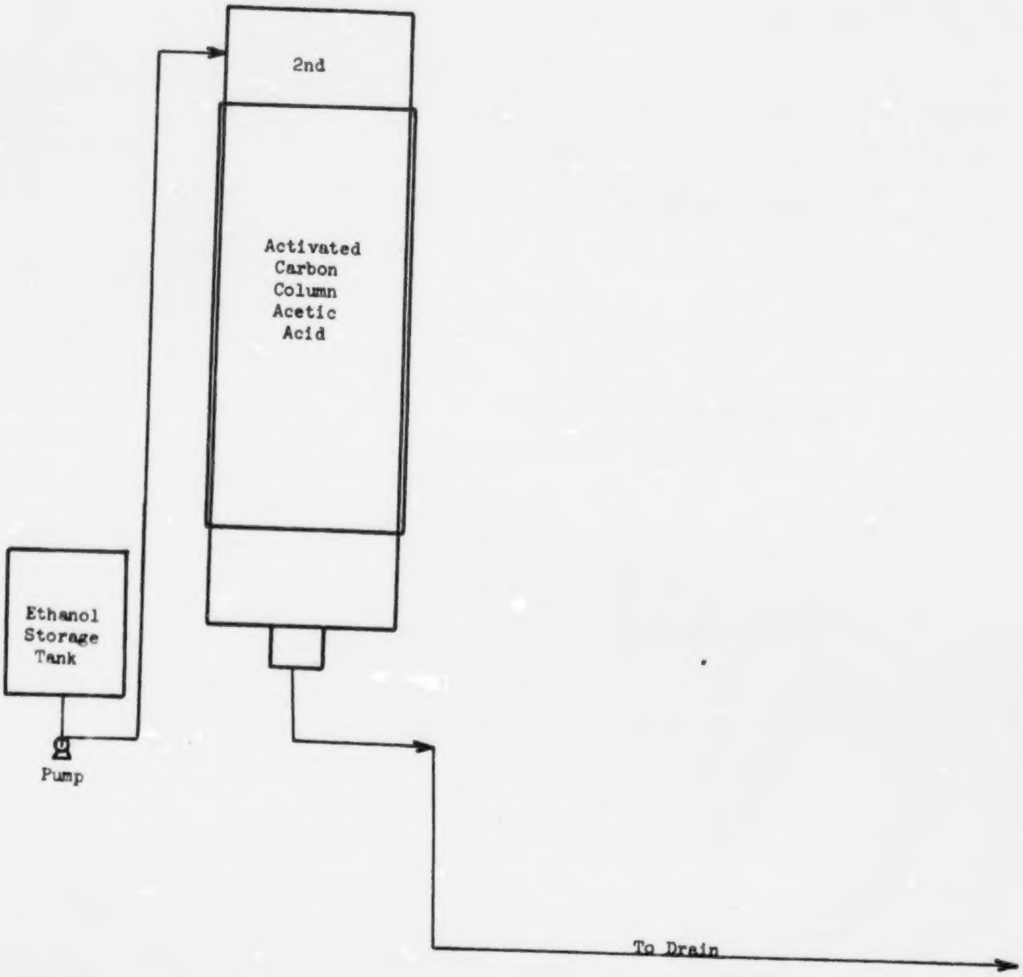
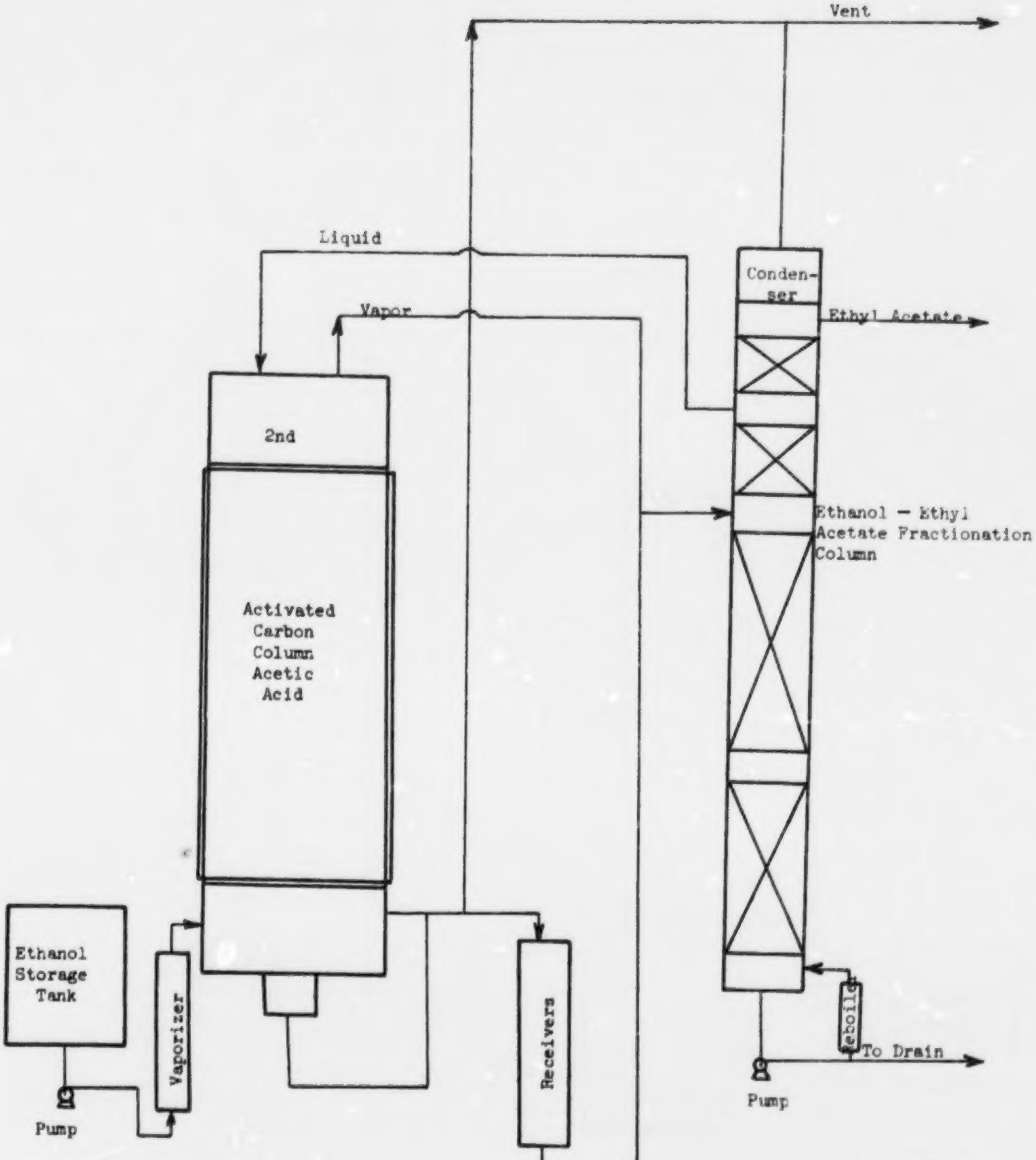

2nd
Activated Carbon Column Acetic Acid
Ethanol Storage Tank
Pump
To Drain

Figure 35. Regeneration – step 1



Vent
Liquid
Vapor
Condenser
Ethyl Acetate
2nd
Activated Carbon Column Acetic Acid
Ethanol – Ethyl Acetate Fractionation Column
Ethanol Storage Tank
Vaporizer
Receivers
Reboiler
To Drain
Pump
Pump
Pump

Figure 36. Regeneration – step 2

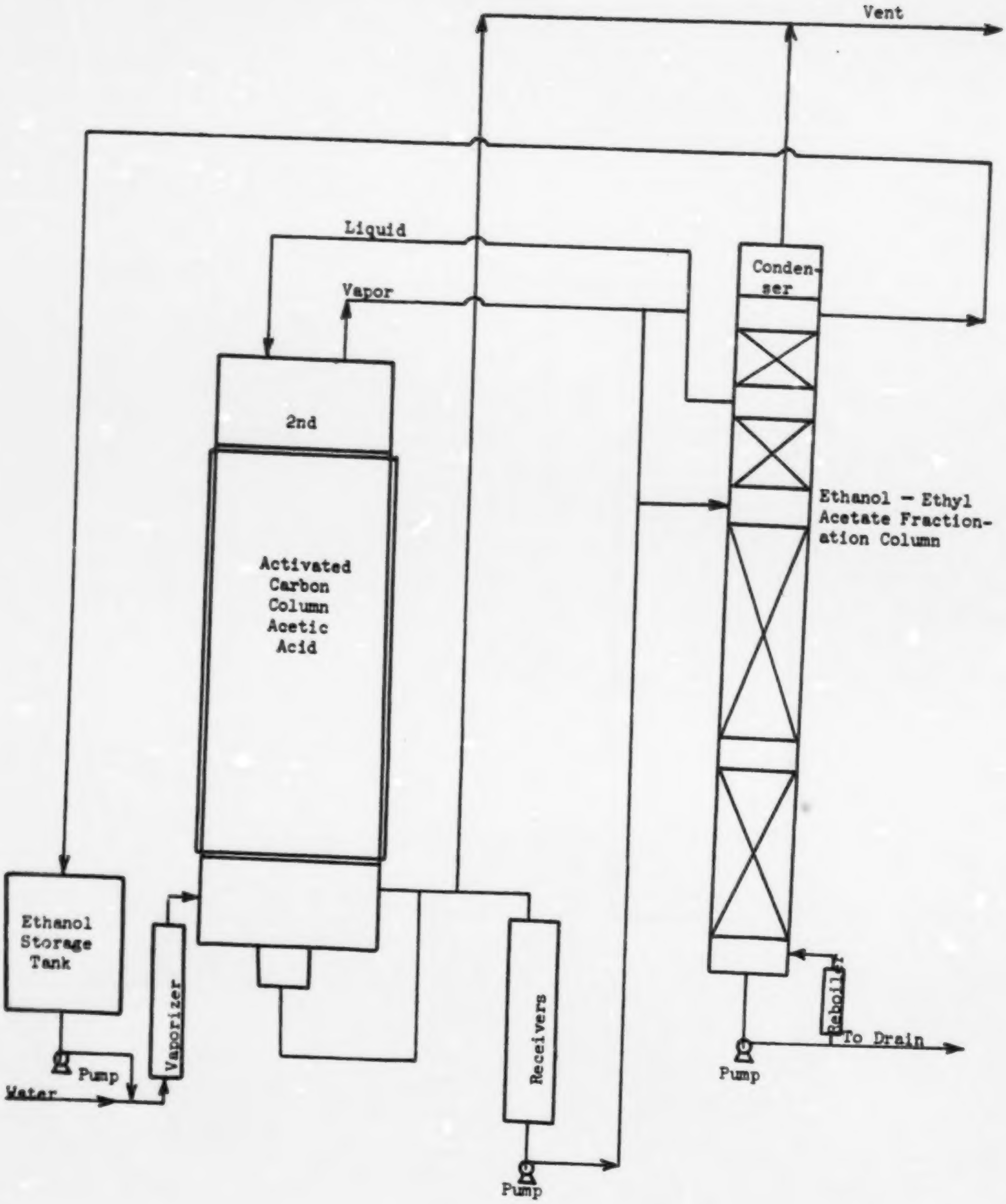

Vent
Liquid
Vapor
Condenser
2nd
Activated Carbon Column Acetic Acid
Ethanol – Ethyl Acetate Fractionation Column
Ethanol Storage Tank
Vaporizer
Pump
Water
Receivers
Pump
Reboiler
To Drain
Pump

Figure 37. Regeneration – step 3

extent that more steam leaked by the original steam pressure regulator than was required now to vaporize the ethanol. A smaller pressure regulator was installed. The ethanol held in the system was reduced tc 10 gal. (37.9 l) from the 40 (151.5) previously used, and the ethanol rate was 0.05 gpm (0.18 l/min.) instead of 0.30 gpm (1.14 l/min.). This necessitated the installation of smaller rotameters. A successful ethanol-water run was made establishing operating parameters during the week of April 2-6, 1973. These operating parameters (see Table 13) were the basis for the newly developed, possibly patentable activated carbon regeneration system.

On April 10, 1973 a steam stripping and activated carbon adsorption run was made. Samples of the acetic acid carbon column effluent were taken after one hour of operation and then every half-hour until a total of 3-1/2 hours adsorption time had elapsed. The feed rate was 1 gpm (3.79 l/min.). The results shown on Fig. 38 were interesting in that no acetic acid was detected in any sample. Previously acetic acid was found in the samples after 2-1/2 hours of adsorption operation and had completely broken through after 3 hours. This indicated the new regeneration system was very effective, and the piping changes may have provided better liquid distribution over the carbon, thereby getting better adsorption.

Unfortunately, during the regeneration run the new by-pass valve to the vent was left open. All the alcohol vaporized, other than that pumped into the column as a liquid, by-passed the carbon column and discharged through the vent. Ethyl acetate was made as the alcohol in the system was vaporized; however, it also worked its way into the recirculation system and was vented. Since it was impossible to tell whether or not the carbon had been regenerated, this regeneration run was repeated. Interestingly very little ethyl acetate was made during the repeat run, indicating either the alcohol in the carbon column was sufficient to regenerate the carbon in the previous regeneration test, or the new regeneration system was ineffective as far as producing ethyl acetate.

Table 13. TYPICAL ACTIVATED CARBON ACETIC ACID COLUMN REGENERATION DATA — POTENTIALLY PATENTABLE PROCESS

Fractionation Column Reboiler, 1st Pressure Gage	—	21 psig	(1.47 kg/cm²)
Fractionation Column Reboiler, 2nd Pressure Gage	—	20 psig	(1.40 kg/cm²)
Fractionation Column Bottom Pressure Gage	—	10" H_2O	(25.4 cm H_2O)
Fractionation Column Feed Station Pressure Gage	—	3" H_2O	(7.6 cm H_2O)
Fractionation Column Middle Splitter Pressure Gage	—	0" H_2O	
Fractionation Column Top Splitter Pressure Gage	—	0" H_2O	
Fractionation Column Vent Pressure Gage	—	0 to ½" H_2O	(0 to 1.8 cm H_2O)
Acetic Acid Activated Carbon Column Top Pressure Gage	—	0 psig	
Acetic Acid Activated Carbon Column Jacket Pressure Gage	—	0 psig	
Acetic Acid Activated Carbon Column Bottom Pressure Gage	—	1¼ psig	(0.12 kg/cm²)
Acetic Acid Activated Carbon Column Vaporizer Pressure Gage	—	16.5 psig	(1.16 kg/cm²)
Acetic Acid Activated Carbon Column Rotameter to Vaporizer	—	0.05 gpm	(0.19 l/min.)
Acetic Acid Activated Carbon Column Rotameter to Fractionator	—	0.05 gpm	(0.19 l/min.)
Temperatures			
Fractionation Column Liquid Bottoms	—	213°F	(100.5°C)
Fractionation Column Bottom Splitter	—	212°F	(100.0°C)
Fractionation Column Feed	—	174°F	(78.9°C)
Fractionation Column Middle Splitter	—	173°F	(78.3°C)
Fractionation Column at Feed Plate	—	174°F	(78.9°C)
Fractionation Column at Top Splitter	—	164°F	(73.3°C)
Fractionation Column Vapor after Condenser	—	92°F	(33.3°C)
Fractionation Column Reboiler Discharge	—	213°F	(100.5°C)
Acetic Acid Activated Carbon Column Top	—	175°F	(79.4°C)
Acetic Acid Activated Carbon Column Bottom	—	207°F	(97.2°C)

Ethyl Acetate Removed Top Fractionator Splitter Periodically

Ethyl Alcohol Removed Bottom Fractionator Splitter to 50 gal. Drain Periodically, 189 liters

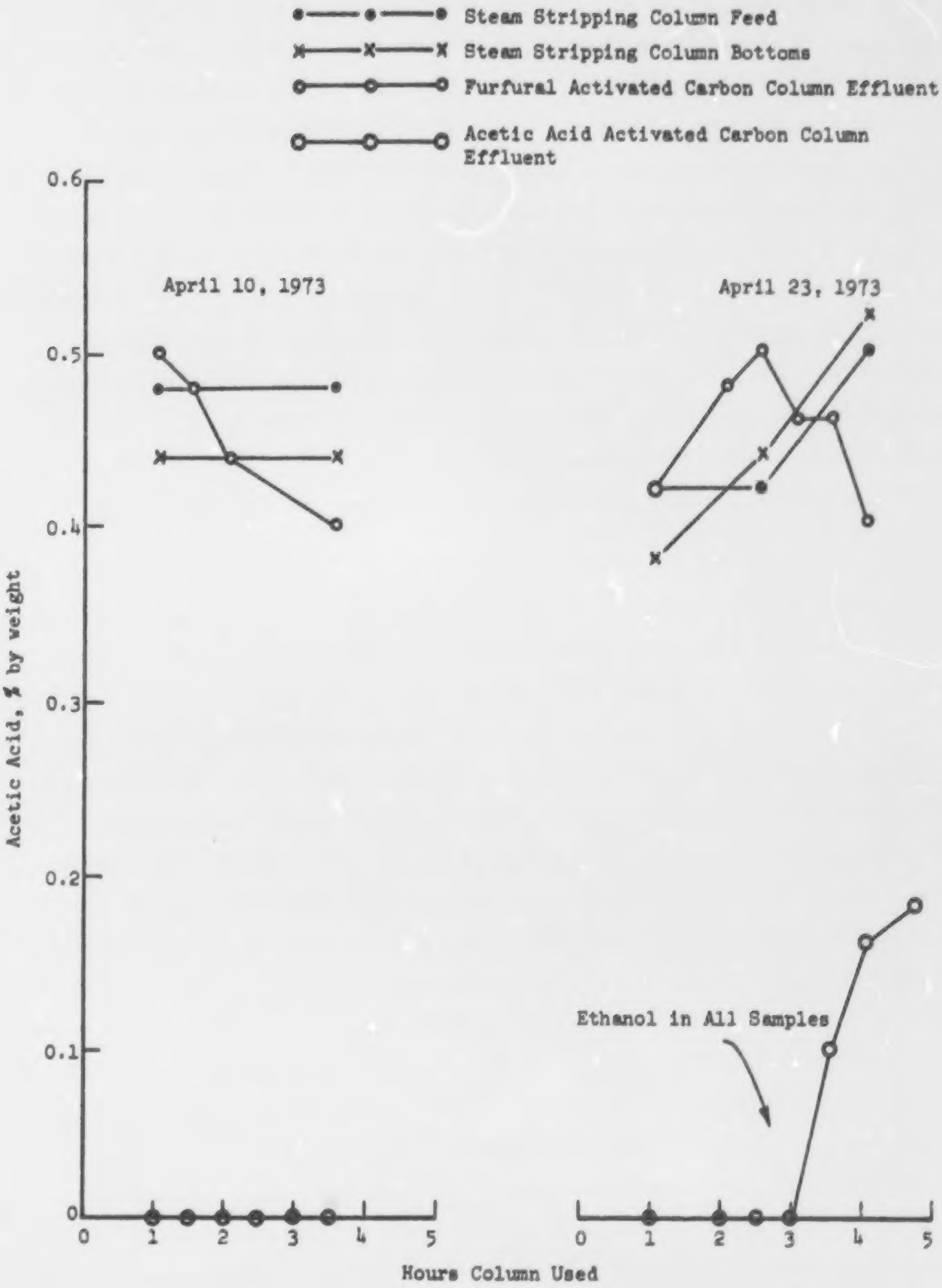


Figure 38. Steam stripping, furfural activated carbon and acetic acid activated carbon columns

The next steam stripping and carbon adsorption run was made April 23, 1973. The evaporator condensate was fed at the rate of 1 gpm (3.79 l/min.) into the steam stripping column. Once again samples of the acetic acid activated carbon column effluent were taken at the end of the first hour and every half hour thereafter for 4 hours total. No acetic acid was detected in the samples after 3 hours, a trace amount in the 3-1/2-hour sample and only 30% by weight of that in the feed in the 4-hour sample. See Fig. 38. These results indicate that the new regeneration method does an efficient job regenerating the carbon. There was still no evidence that the acetic acid was being effectively removed as ethyl acetate. Since all effluent samples showed ethanol, it was obvious the regeneration purge of ethanol was stopped prematurely. The previous run had shown an excellent purge of ethanol, so this is no problem.

Another regeneration attempt to verify the production of ethyl acetate was made on April 24, 1973. This time the odor of ethyl acetate was strongly detected. A check for leakage was to no avail. Finally, the pipe from the steam trap taking care of condensed steam from the activated carbon vaporizer and jacket was disconnected from the drain. The ethanol and ethyl acetate coming from the pipe was of high concentration, indicating a leak in the reboiler or the jacket. The two systems were separated and the leak was pin-pointed as being in the jacket. Analyses of the water discharging from the carbon column and finally leaving the bottom of the fractionation column showed 0.03% by weight acetic acid, indicating little loss as acetic acid. The run was continued April 25, 1973 to verify the removal of acetic acid as ethyl acetate. Approximately 2 quarts (1.9 liters) of 50%+ by weight ethyl acetate were collected. Once the analyses showed sufficient ethyl acetate was made, the regeneration was stopped, as the regeneration method was shown effective and there was no need to risk further column damage. The activated carbon was removed from the column. Inspection showed that the inner shell of the column was pushed in opposite the steam inlet to the jacket. A hole was under the convexed section about

3 feet (91.4 cm) from the top of the column. Further checking revealed that the installed pop-off valve was for 70 psig (4.9 kg/cm^2 gage) instead of 7 psig (0.49 kg/cm^2 gage) as was expected. It is probable that during the runs when trouble controlling the steam pressures occurred, the combination of high jacket pressure and a vacuum inside the column occurred simultaneously buckling the inner shell. Since the pop-off valve never released, the high pressure was not revealed. This was the second time the inner column had collapsed, so no attempt was made to repair it.

The new regeneration system appears more complicated than it is. A simplified form is shown in Fig. 39. Essentially, the system involves using the activated carbon column as a distillation column during the carbon regeneration cycle. A smaller fractionation column is added to the top of the carbon column for product purity improvement. This may, or may not, be required. Alcohol (ethanol is used) is pumped into the carbon column below the fractionation column and above the activated carbon. Water containing acetic acid, polymerized material, and portions of spent sulfite liquor comes out the bottom of the carbon column, and is collected in the receivers. From there it is recirculated by means of a pump through a vaporizer and disengaging section at the bottom of the carbon column. The vapor from the partially vaporized recirculating liquor passes up the carbon column. By controlling the heat to the vaporizer the carbon column is gradually converted into a reactor and distillation column. As the vapors move up the column, water condenses and is displaced, while the alcohol vaporizes and reacts with the acetic acid to form esters (ethyl acetate). As the alcohol and acetate are rectified at the top of the carbon column and in the fractionation column by means of refluxing the condensed overhead vapors, the water containing furfural, polymerized material, and residual spent sulfite liquor are collected in the receivers. Once all the acetic acid has been converted to ethyl acetate, the alcohol is recovered by vaporizing the recirculating liquor and concentrating the collected materials in it.

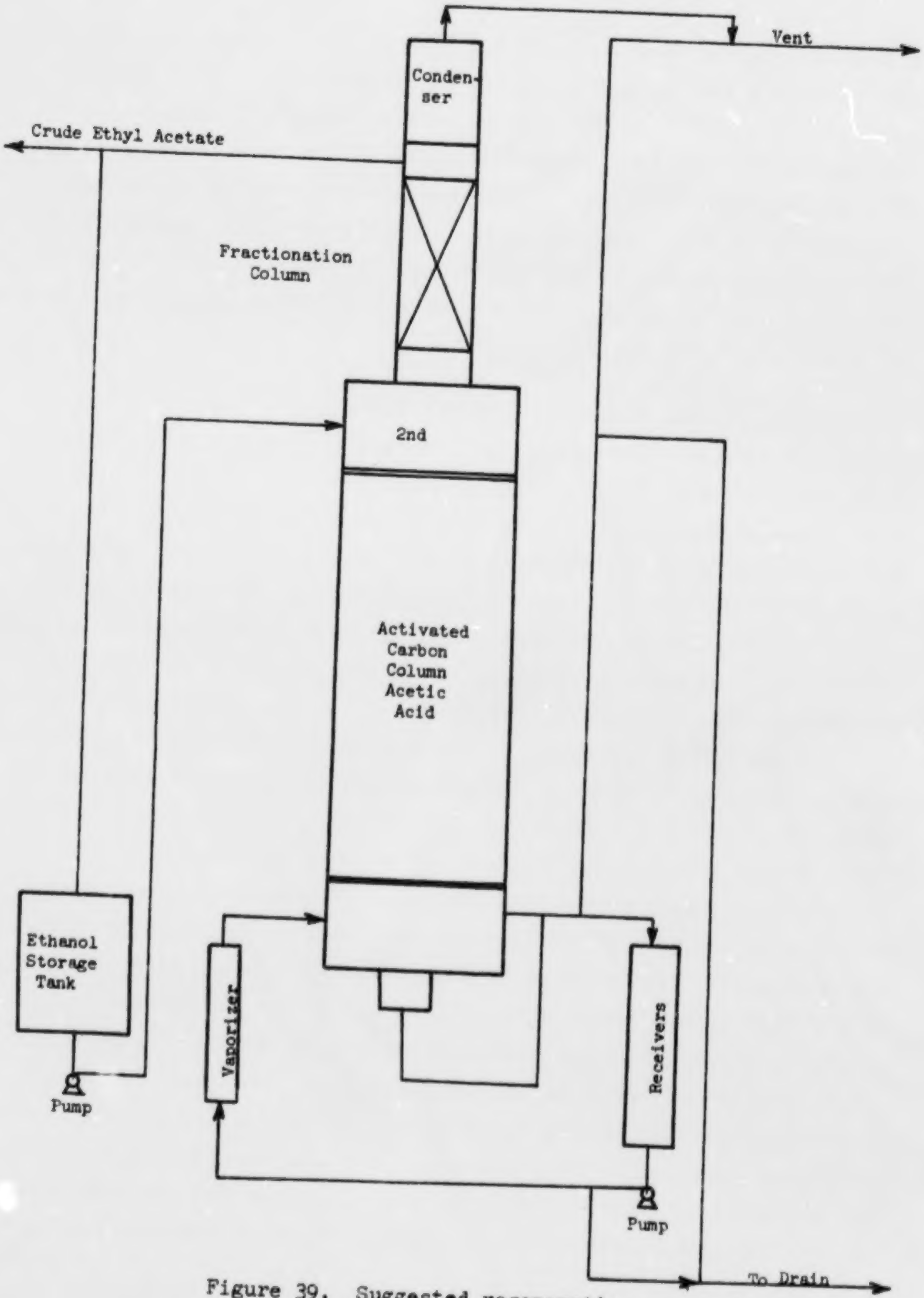

Vent
Conden-
ser
Crude Ethyl Acetate
Fractionation
Column
2nd
Activated
Carbon
Column
Acetic
Acid
Ethanol
Storage
Tank
Pump
Vaporizer
Receivers
Pump
To Drain

Figure 39. Suggested regeneration

When only steam remains in the carbon column, it is ready for its next adsorption cycle.

Figures 40 and 41 show the application of what was learned in this project used as the bases to project the utilization of the developed unit operations for clarifying evaporator condensate at Consolidated Papers, Inc.'s Appleton Mill.

Present Project Status

During Project 3100 enough data were compiled to assist interested sulfite pulp manufacturers toward making feasibility studies for utilizing steam stripping, fractionation, and activated carbon adsorption systems as tools toward solving their pollution problems. The major project achievements were:

1. The development of a steam stripping system capable of removing 90%+ by weight of the sulfur dioxide in evaporator condensates. Only the evaporator condensate data for interested mills need be established to effectively design this system.
2. The fractionation system developed and patented by Scott Paper Company was optimized. This system is capable of producing high purity sulfur dioxide for reuse back in the mill, methanol for reuse and eventual sale, and furfural for sale.
3. The verification of selective activated carbon adsorption data compiled at Scott Paper Company and used as the bases for their selective adsorption patent. Carbon loadings were established.
4. An activated carbon regeneration system capable of producing a high purity ethyl acetate crude (89% by weight ethyl acetate) from adsorbed acetic acid was demonstrated.
5. The use of alcohol and water for regenerating the activated carbon when using relatively clean evaporator condensate was shown to be effective. The carbon life showed signs of deteriorating when dirty evaporator condensate was processed, and the carbon was regenerated

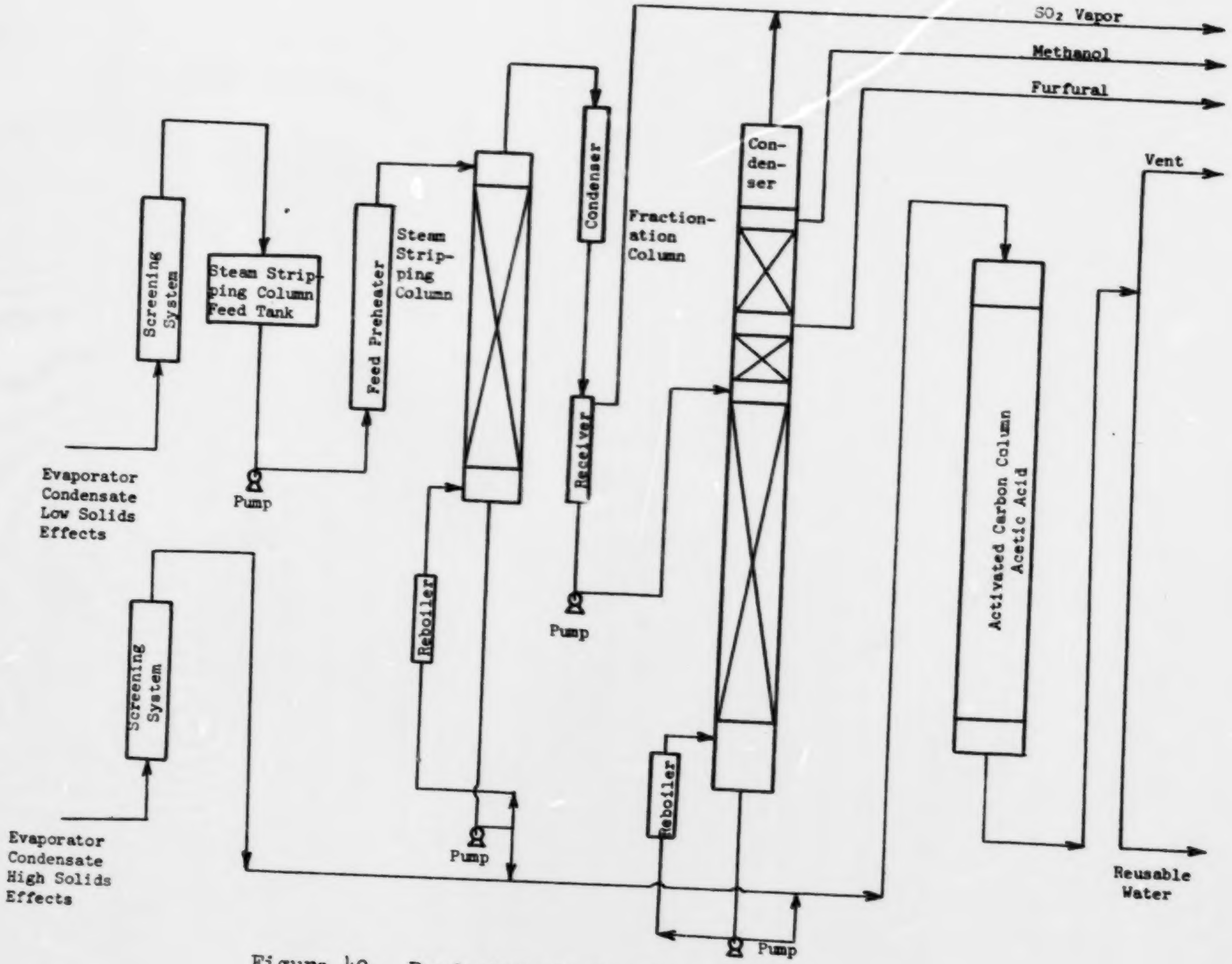

Evaporator Condensate Low Solids Effects
Screening System
Steam Stripping Column Feed Tank
Pump
Feed Preheater
Steam Stripping Column
Reboiler
Pump
Condenser
Receiver
Pump
Fractionation Column
Condenser
Reboiler
Pump
SO₂ Vapor
Methanol
Furfural
Vent
Activated Carbon Column Acetic Acid
Reusable Water
Evaporator Condensate High Solids Effects
Screening System

Figure 40. Projected plant — Consolidated Papers, Inc.
Appleton mill

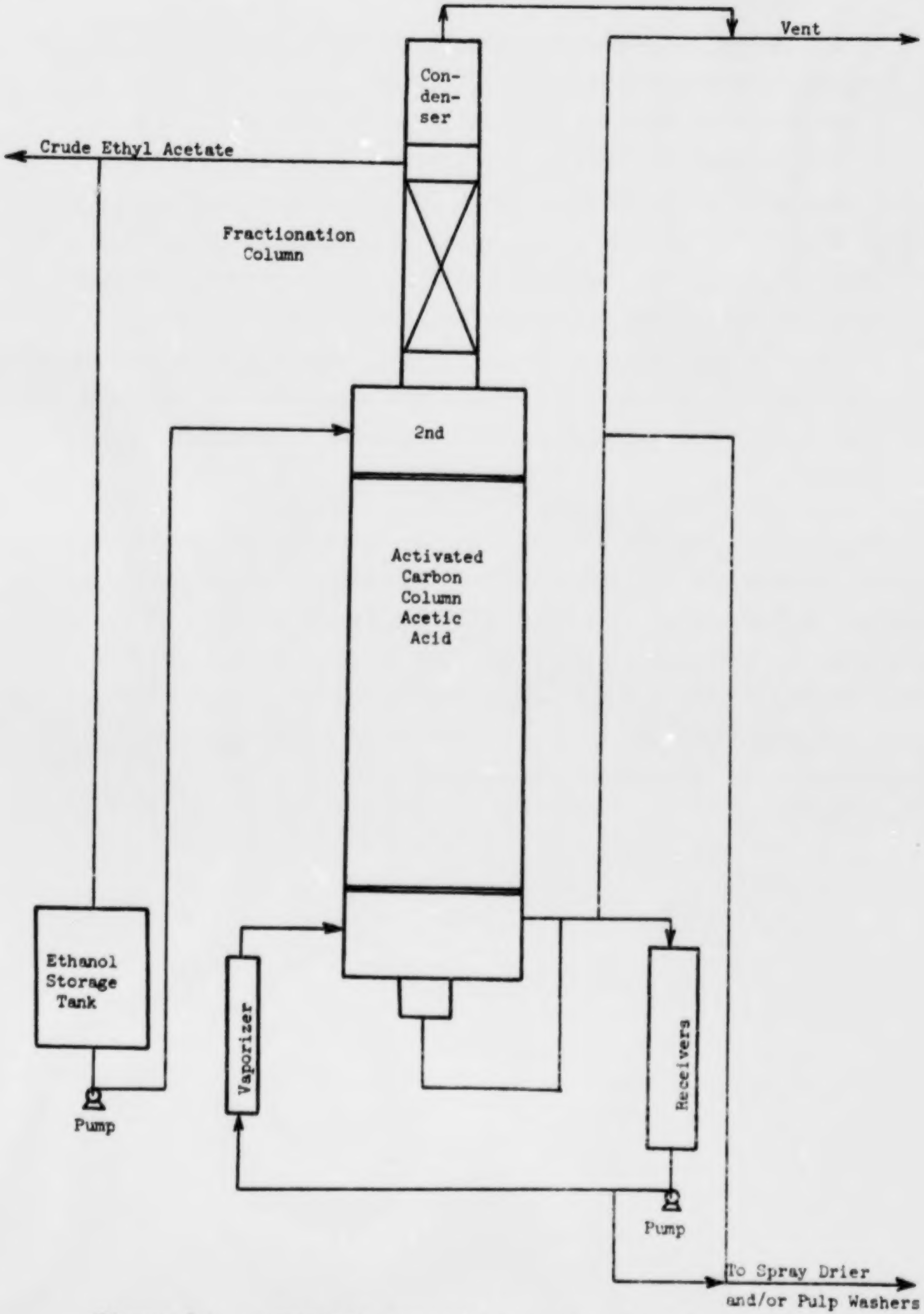

Vent
Con-
den-
ser
Crude Ethyl Acetate
Fractionation
Column
2nd
Activated
Carbon
Column
Acetic
Acid
Ethanol
Storage
Tank
Pump
Vaporizer
Receivers
Pump
To Spray Drier
and/or Pulp Washers

Figure 41. Suggested commercial application Consolidated Papers, Inc. Appleton mill

by the system developed and patented at Scott Paper Company. These regeneration systems were not optimized.

6. A new activated carbon regeneration system was developed using alcohol and water. This system involves using the activated carbon column as a distillation column. It varies from the Scott method in that reflux of alcohol and water is utilized in the carbon column. It completely regenerated a carbon that had been showing definite carbon life deterioration, and may be patentable. This process has not been optimized, although substantial cost reductions when compared to the Scott process are apparent. Data on this process are limited and more work is necessary to establish its full value.

The urgency required for pollution abatement is the factor most influencing the movement of this project to commercialization in its entirety. The next step is a commercial demonstration unit. Preferably it should be constructed modularly. The steam stripping and fractionation systems first, and the carbon adsorption and regeneration systems next. The highest priority pilot plant study should generate data specifically for this demonstration unit.

SECTION VI

MASS, HEAT, AND BOD_5 BALANCES

METHODOLOGY

Mass, heat and BOD_5 balances are made according to the actual operating condition of the pilot plant at the Appleton Division Mill of Consolidated Papers, Inc. and are based on data taken prior to January 17, 1973. See Tables 14, 15, and 16. Since the individual items of the equipment are not optimized and this general process may not be particularly exact for the evaporator condensate processed, it is believed that total energy balances of this pilot plant would be of little value and could be misleading. Only heat balances are made. From this basic information, an estimate of the value of the products was obtained.

A pollutional balance sheet is also included. This sheet shows the BOD_5 values of the flow streams shown in the overall mass balances of the pilot plant (Fig. 42). The references for those theoretical conversions are also listed.

The balances presented are for the particular arrangement which was studied during these experiments. The particulars of product value, equipment arrangement, and operating costs for other evaporator systems will, of course, be somewhat different depending upon the individual pulp mill's opportunities and major objectives in the installation of this process.

MASS BALANCES

The mass flows are shown in six separate mass-flow sheets: Figure 43 covers the separation process; Fig. 44 and 45, the recovery of furfural and methanol; and Fig. 46 and 47, the recovery of ethyl acetate and ethanol. The three operations are then combined as Fig. 42 which shows the overall mass balances of the complete process.

Table 14. TYPICAL PILOT-PLANT OPERATING DATA

Evaporator Condensate Transfer Pump Rotameter Reading	— 20	
Evaporator Condensate Transfer Pump Pressure Gage	— 15 psig	(1.05 kg/cm^2)
Steam Stripper Feed Tank Level	— Full	
Steam Stripper Feed Pressure Gage	— 41 psig	(2.88 kg/cm^2)
Steam Stripper Feed Rotameter — 67%	— 1 gpm	(3.79 l/min.)
Steam Stripper Steam Rotameter — 10 setting	— 0.060 gpm	(0.23 l/min.)
Steam Stripper Manometer	— 0" H_2O	(0 cm H_2O)
Main Line Steam Pressure Gage	— 130 psig	(9.14 kg/cm^2)
Preheater, 1st Pressure Gage	— 130 psig	(9.14 kg/cm^2)
Preheater, 2nd Pressure Gage	— 73 psig	(5.13 kg/cm^2)
Preheater, Dial Thermometer	— 211°F	(99.4°C)
Reboiler, 1st Pressure Gage	— 83 psig	(5.83 kg/cm^2)
Reboiler, 2nd Pressure Gage	— 52 psig	(3.65 kg/cm^2)
Steam Stripping Column Top Pressure Gage	— No good	
Steam Stripping Column Bottom Pressure Gage	— 7.4" H_2O	(18.8 cm H_2O)
Water to Steam Stripping Column Condenser Rotameter	— 7.5 Setting	
Steam Stripping Column Condensed Overhead Rotameter, 9.5	— 0.057 gpm	(0.22 l/min.)
Fractionation Column Reboiler Rotameter — 8.5 setting	— 0.049 gpm	(0.18 l/min.)
Fractionation Column Steam, 1st Pressure Gage	— 135 psig	(9.49 kg/cm^2)
Fractionation Column Steam, 2nd Pressure Gage	— 125 psig	(8.79 kg/cm^2)
Fractionation Column Bottom Pressure Gage	— 0" H_2O	(0 cm H_2O)
Fractionation Column Manometer (Feed to Bottom)	— 0.3" H_2O	(0.76 cm H_2O)
Fractionation Column Top Pressure Gage	— 2.5" H_2O	(6.35 cm H_2O)
Furfural Activated Carbon Column Feed Pressure Gage	— 18 psig	(1.26 kg/cm^2)
Furfural Activated Carbon Column Feed Rotameter	— 1.06 gpm	(4.01 l/min.)
Furfural Activated Carbon Column Bottom Pressure Gage	— 5 psig	(0.35 kg/cm^2)
Furfural Activated Carbon Column Top Pressure Gage	— 4 psig	(0.28 kg/cm^2)
Acetic Acid Activated Carbon Column Top Pressure Gage	— 4 psig	(0.28 kg/cm^2)
Acetic Acid Activated Carbon Column Bottom Pressure Gage	— 6.7 psig	(0.47 kg/cm^2)

Temperatures

Steam Stripping Column Feed before Preheater	— 134°F	(56.7°C)
Steam Stripping Column Feed after Preheater	— 212°F	(100.0°C)
Steam Stripping Column Liquid Bottoms	— 212°F	(100.0°C)
Steam Stripping Column Top Vapor	— 213°F	(100.6°C)
Steam Stripping Column Vapor after Condenser	— 203°F	(95.0°C)
Steam Stripping Column Steam	— 247°F	(119.4°C)
Fractionation Column Liquid Bottoms	— 210°F	(98.9°C)
Fractionation Column Steam	— 213°F	(100.6°C)
Fractionation Column Feed	— 166°F	(74.4°C)
Fractionation Column at Feed Plate	— 213°F	(100.6°C)
Fractionation Column 1st Splitter	— 213°F	(100.6°C)
Fractionation Column 2nd Splitter	— 149°F	(65.0°C)
Fractionation Column Vapor after Condenser	— 97°F	(36.1°C)
Activated Carbon Column Bottom (Furfural)	— 140°F	(60.0°C)
Activated Carbon Column Center (Furfural)	— 140°F	(60.0°C)
Activated Carbon Column Top	— 135°F	(57.2°C)
Activated Carbon Column Bottom (Acetic Acid)	— 129°F	(53.9°C)
Activated Carbon Column Top (Acetic Acid)	— 133°F	(56.1°C)

Table 15. TYPICAL ACTIVATED CARBON ACETIC ACID COLUMN REGENERATION DATA

Fractionation Column Reboiler, 1st Pressure Gage	—	67 psig	(4.71 kg/cm^2)
Fractionation Column Reboiler, 2nd Pressure Gage	—	66 psig	(4.64 kg/cm^2)
Fractionation Column Bottom Pressure Gage	—	0 psig	(0.00 kg/cm^2)
Fractionation Column Manometer (Feed to Bottom)	—	1" H_2O	(2.54 cm H_2O)
Fractionation Column Top Pressure Gage	—	$2\frac{1}{4}$" H_2O	(6.35 cm H_2O)
Fractionation Column Middle Pressure Gage	—	3" H_2O	(7.62 cm H_2O)
Acetic Acid Activated Carbon Column Top Pressure Gage	—	0 psig	(0.00 kg/cm^2)
Acetic Acid Activated Carbon Column Jacket Steam Pressure	—	4 psig	(0.28 kg/cm^2)
Acetic Acid Activated Carbon Column Bottom Pressure Gage	—	7 psig	(0.49 kg/cm^2)
Acetic Acid Activated Carbon Column Vaporizer 1st Steam Pressure Gage	—	135 psig	(9.49 kg/cm^2)
Acetic Acid Activated Carbon Column Vaporizer 2nd Steam Pressure Gage	—	115 psig	(8.08 kg/cm^2)
Acetic Acid Activated Carbon Column Rotameter to Acetic Carbon Column	—	0.30 gpm	(1.14 l/min.)
Acetic Acid Activated Carbon Column Fractionator (Alcohol)	—	0.30 gpm	(1.14 l/min.)
Temperatures			
Fractionation Column Liquid Bottoms	—	212°F	(100.0°C)
Fractionation Column Steam	—	213°F	(100.6°C)
Fractionation Column Bottom Splitter	—	173°F	(78.3°C)
Fractionation Column Feed	—	174°F	(78.9°C)
Fractionation Column at Feed Plate	—	172°F	(77.8°C)
Fractionation Column at Middle Splitter	—	162°F	(72.2°C)
Fractionation Column at Top Splitter	—	157°F	(69.4°C)
Fractionation Column Vapor after Condenser	—	100°F	(37.8°C)
Acetic Acid Activated Carbon Column Top	—	175°F	(79.4°C)
Acetic Acid Activated Carbon Column Bottom	—	173°F	(78.3°C)

Table 16. TYPICAL ACTIVATED CARBON FURFURAL COLUMN REGENERATION DATA

Fractionation Column Reboiler, 1st Pressure Gage	–	70 psig	(4.92 kg/cm^2)
Fractionation Column Reboiler, 2nd Pressure Gage	–	67 psig	(4.71 kg/cm^2)
Fractionation Column Bottom Pressure Gage	–	0 psig	(0.00 kg/cm^2)
Fractionation Column Manometer (Feed to Bottom)	–	1" H_2O	(2.54 cm H_2O)
Fractionation Column Top Pressure Gage	–	2½" H_2O	(6.35 cm H_2O)
Fractionation Column Middle Pressure Gage	–	3" H_2O	(7.62 cm H_2O)
Activated Carbon Furfural Column Top Pressure Gage	–	3 psig	(0.21 kg/cm^2)
Activated Carbon Furfural Column Bottom Pressure Gage	–	0 psig	(0.00 kg/cm^2)
Temperatures			
Fractionation Column Liquid Bottoms	–	213°F	(100.6°C)
Fractionation Column Bottom Splitter	–	149°F	(65.0°C)
Fractionation Column Feed	–	149°F	(65.0°C)
Fractionation Column at Feed Plate	–	150°F	(65.6°C)
Fractionation Column Middle Splitter	–	149°F	(65.0°C)
Fractionation Column Top Splitter	–	149°F	(65.0°C)
Fractionation Column Vent	–	96°F	(35.6°C)
Activated Carbon Furfural Column Bottom	–	147°F	(63.9°C)
Activated Carbon Furfural Column Middle	–	147°F	(63.9°C)
Activated Carbon Furfural Column Top	–	151°F	(66.1°C)
Flow Rates to Activated Carbon Column	–	0.10 gpm	(0.38 l/min.)
Flow Rates to Fractionation Column	–	0.10 gpm	(0.38 l/min.)

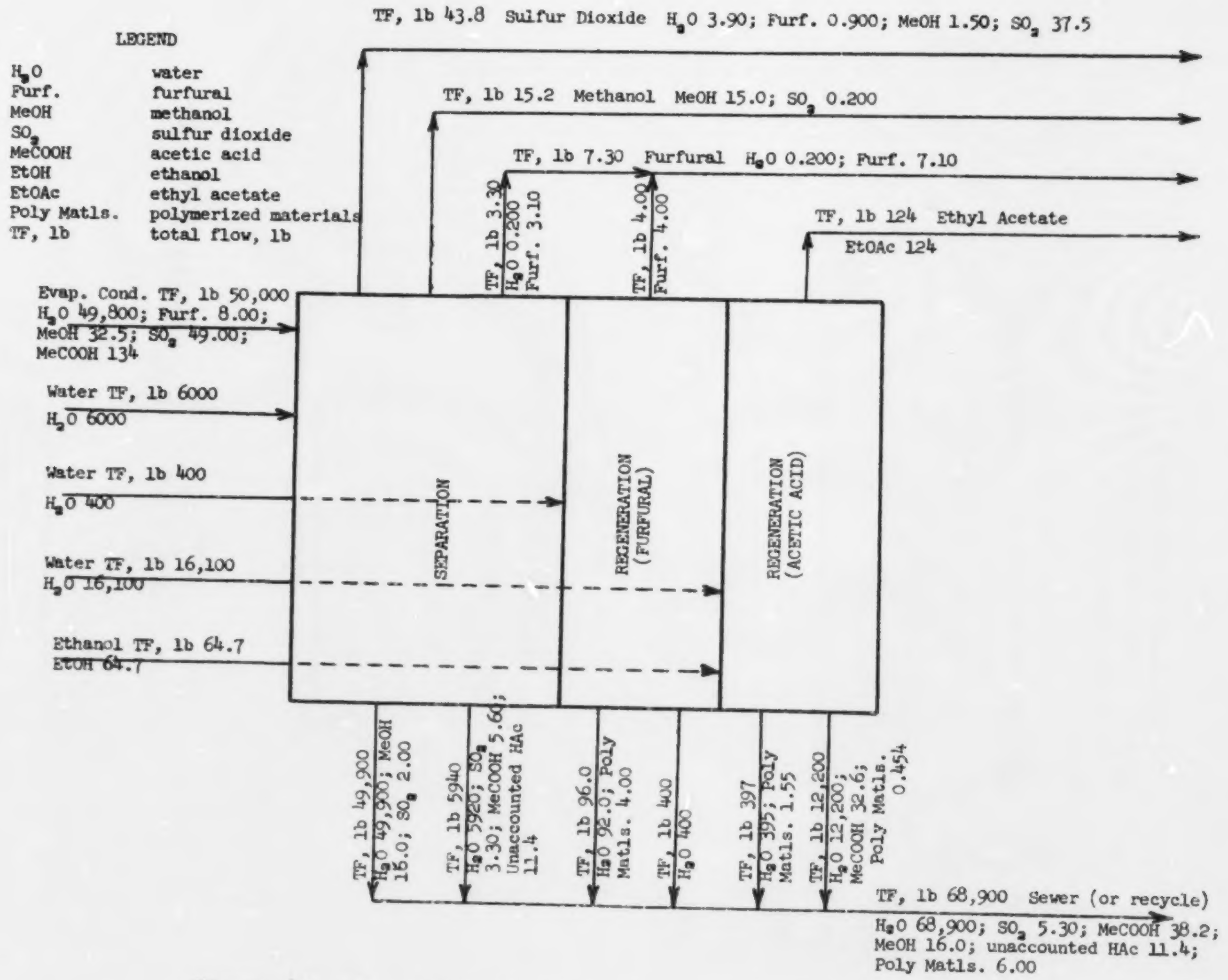

LEGEND
H_2O water
Furf. furfural
MeOH methanol
SO_2 sulfur dioxide
MeCOOH acetic acid
EtOH ethanol
EtOAc ethyl acetate
Poly Matls. polymerized materials
TF, lb total flow, lb
TF, lb 43.8 Sulfur Dioxide H_2O 3.90; Furf. 0.900; MeOH 1.50; SO_2 37.5
TF, lb 15.2 Methanol MeOH 15.0; SO_2 0.200
TF, lb 7.30 Furfural H_2O 0.200; Furf. 7.10
TF, lb 3.30 H_2O 0.200 Furf. 3.10
TF, lb 4.00 Furf. 4.00
TF, lb 124 Ethyl Acetate EtOAc 124
Evap. Cond. TF, lb 50,000 H_2O 49,800; Furf. 8.00; MeOH 32.5; SO_2 49.00; MeCOOH 134
Water TF, lb 6000 H_2O 6000
Water TF, lb 400 H_2O 400
Water TF, lb 16,100 H_2O 16,100
Ethanol TF, lb 64.7 EtOH 64.7
SEPARATION
REGENERATION (FURFURAL)
REGENERATION (ACETIC ACID)
TF, lb 49,900 H_2O 49,900; MeOH 18.0; SO_2 2.00
TF, lb 5940 H_2O 5920; SO_2 3.30; MeCOOH 5.60; Unaccounted HAc 11.4
TF, lb 96.0 H_2O 92.0; Poly Matls. 4.00
TF, lb 400 H_2O 400
TF, lb 397 H_2O 395; Poly Matls. 1.55
TF, lb 12,200 H_2O 12,200; MeCOOH 32.6; Poly Matls. 0.454
TF, lb 68,900 Sewer (or recycle)
H_2O 68,900; SO_2 5.30; MeCOOH 38.2; MeOH 16.0; unaccounted HAc 11.4; Poly Matls. 6.00

Figure 42. Overall mass balances of the pilot plant

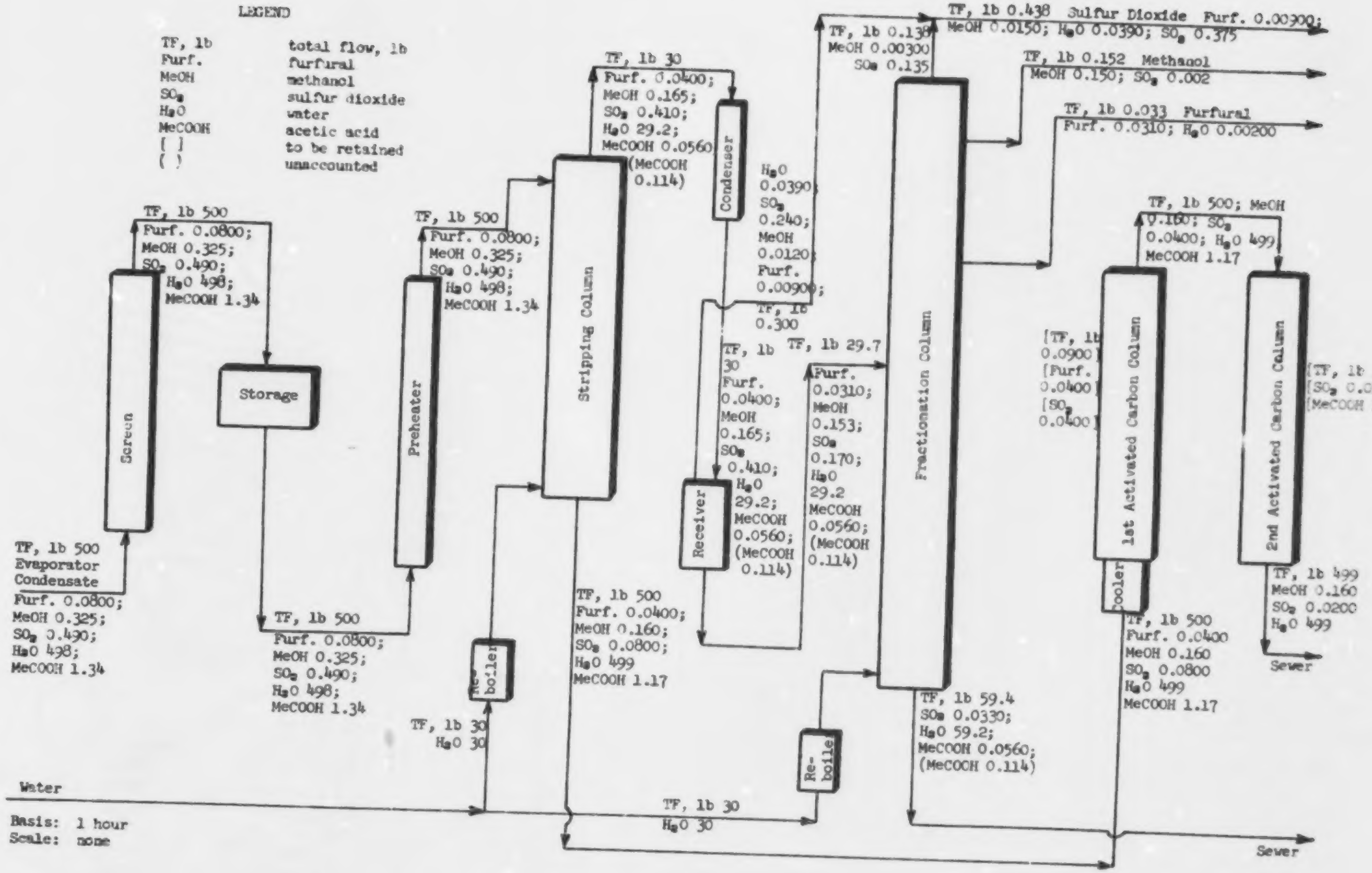
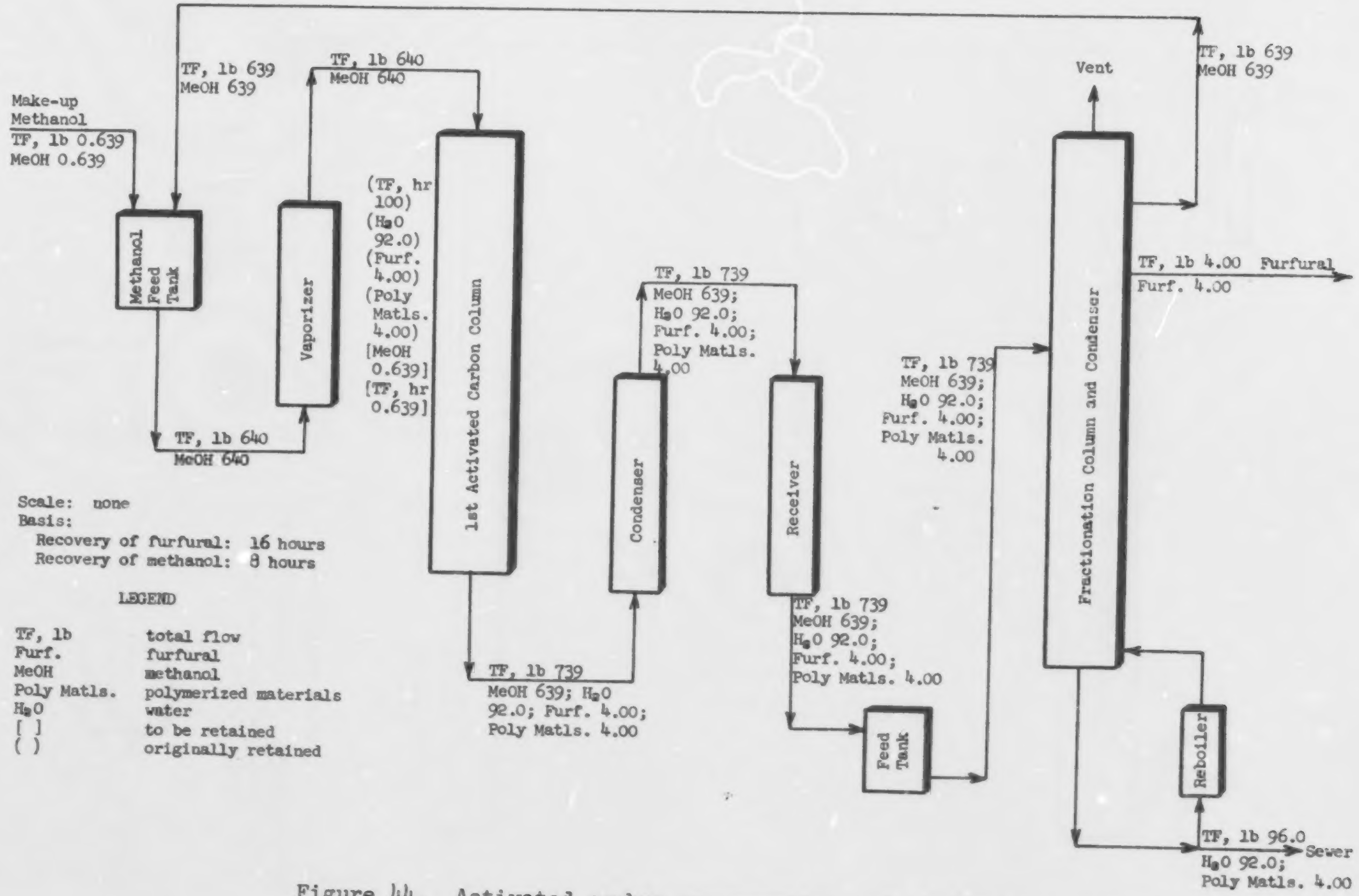

LEGEND
TF, lb total flow, lb
Furf. furfural
MeOH methanol
SO_2 sulfur dioxide
H_2O water
MeCOOH acetic acid
[ ] to be retained
( ) unaccounted
Screen
Storage
Preheater
Stripping Column
Condenser
Receiver
Fractionation Column
1st Activated Carbon Column
Cooler
2nd Activated Carbon Column
Re-boiler
Re-boile
TF, lb 500 Evaporator Condensate Furf. 0.0800; MeOH 0.325; SO_2 0.490; H_2O 498; MeCOOH 1.34
TF, lb 500 Furf. 0.0800; MeOH 0.325; SO_2 0.490; H_2O 498; MeCOOH 1.34
TF, lb 500 Furf. 0.0800; MeOH 0.325; SO_2 0.490; H_2O 498; MeCOOH 1.34
TF, lb 500 Furf. 0.0800; MeOH 0.325; SO_2 0.490; H_2O 498; MeCOOH 1.34
TF, lb 30 Furf. 0.0400; MeOH 0.165; SO_2 0.410; H_2O 29.2; MeCOOH 0.0560 (MeCOOH 0.114)
H_2O 0.0390; SO_2 0.240; MeOH 0.0120; Furf. 0.00900; TF, lb 0.300
TF, lb 30 Furf. 0.0400; MeOH 0.165; SO_2 0.410; H_2O 29.2; MeCOOH 0.0560; (MeCOOH 0.114)
TF, lb 29.7 Furf. 0.0310; MeOH 0.153; SO_2 0.170; H_2O 29.2 MeCOOH 0.0560; (MeCOOH 0.114)
TF, lb 0.138 MeOH 0.00300 SO_2 0.135
TF, lb 0.438 Sulfur Dioxide Furf. 0.00900; MeOH 0.0150; H_2O 0.0390; SO_2 0.375
TF, lb 0.152 Methanol MeOH 0.150; SO_2 0.002
TF, lb 0.033 Furfural Furf. 0.0310; H_2O 0.00200
TF, lb 500 Furf. 0.0400; MeOH 0.160; SO_2 0.0800; H_2O 499 MeCOOH 1.17
TF, lb 30 H_2O 30
TF, lb 30 H_2O 30
TF, lb 59.4 SO_2 0.0330; H_2O 59.2; MeCOOH 0.0560; (MeCOOH 0.114)
[TF, lb 0.0900] [Furf. 0.0400] [SO_2 0.0400]
TF, lb 500 Furf. 0.0400 MeOH 0.160 SO_2 0.0800 H_2O 499 MeCOOH 1.17
TF, lb 500; MeOH 0.160; SO_2 0.0400; H_2O 499 MeCOOH 1.17
[TF, lb 1.19] [SO_2 0.0200] [MeCOOH 1.17]
TF, lb 499 MeOH 0.160 SO_2 0.0200 H_2O 499
Sewer
Sewer
Water
Basis: 1 hour
Scale: none

Figure 43. Separation process — mass flow sheet


Make-up
Methanol
TF, lb 0.639
MeOH 0.639
Methanol Feed Tank
TF, lb 639
MeOH 639
TF, lb 640
MeOH 640
Vaporizer
TF, lb 640
MeOH 640
(TF, hr 100)
(H2O 92.0)
(Furf. 4.00)
(Poly Matls. 4.00)
[MeOH 0.639]
[TF, hr 0.639]
1st Activated Carbon Column
TF, lb 739
MeOH 639; H2O 92.0; Furf. 4.00; Poly Matls. 4.00
Condenser
TF, lb 739
MeOH 639; H2O 92.0; Furf. 4.00; Poly Matls. 4.00
Receiver
TF, lb 739
MeOH 639; H2O 92.0; Furf. 4.00; Poly Matls. 4.00
Feed Tank
TF, lb 739
MeOH 639; H2O 92.0; Furf. 4.00; Poly Matls. 4.00
Fractionation Column and Condenser
Vent
TF, lb 639
MeOH 639
TF, lb 4.00 Furfural
Furf. 4.00
Reboiler
TF, lb 96.0
H2O 92.0;
Poly Matls. 4.00
Sewer

Scale: none
Basis:
Recovery of furfural: 16 hours
Recovery of methanol: 8 hours

LEGEND

TF, lb	total flow
Furf.	furfural
MeOH	methanol
Poly Matls.	polymerized materials
H_2O	water
[ ]	to be retained
( )	originally retained

Figure 44. Activated carbon regeneration and furfural recovery.
1. Furfural recovery

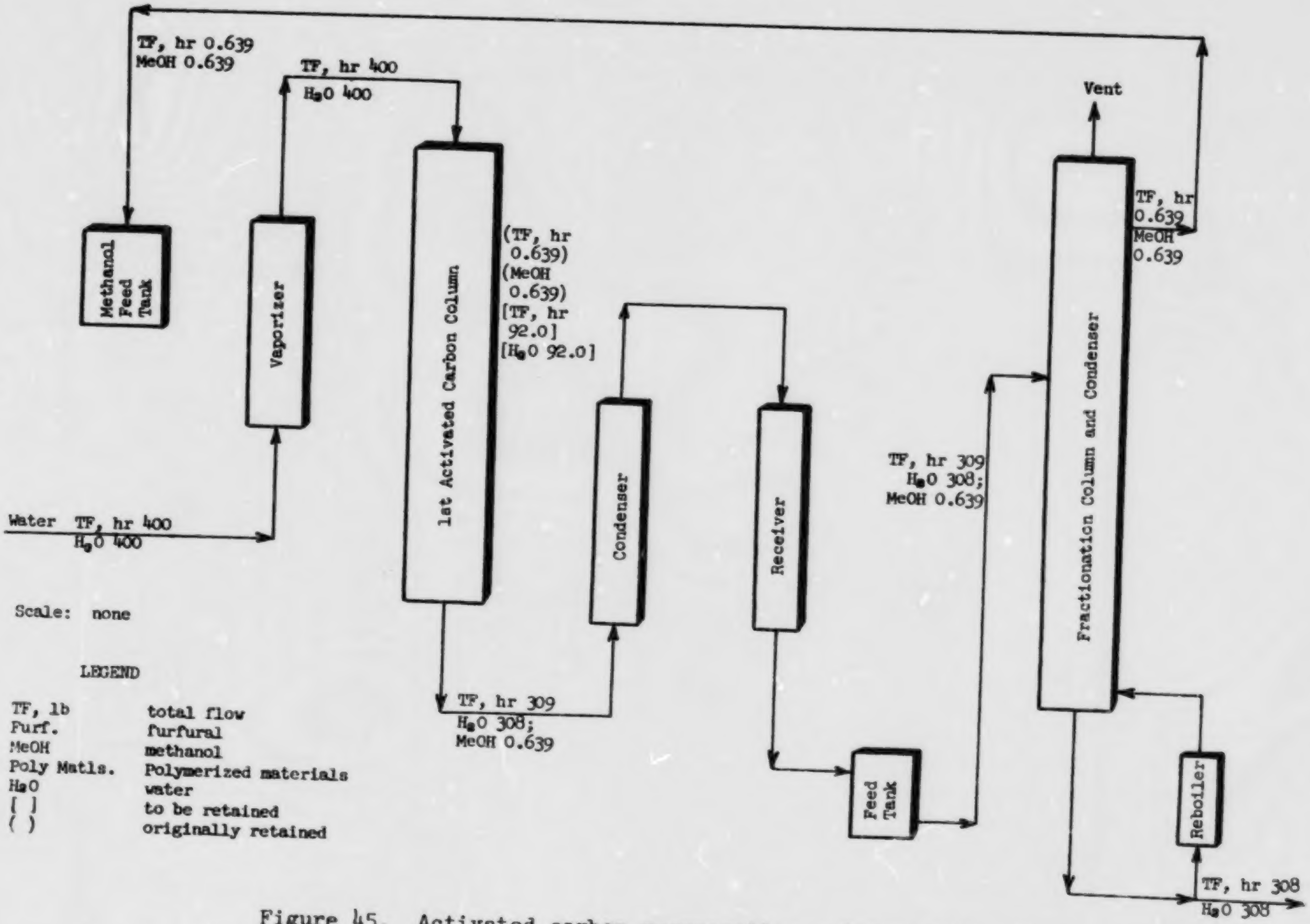
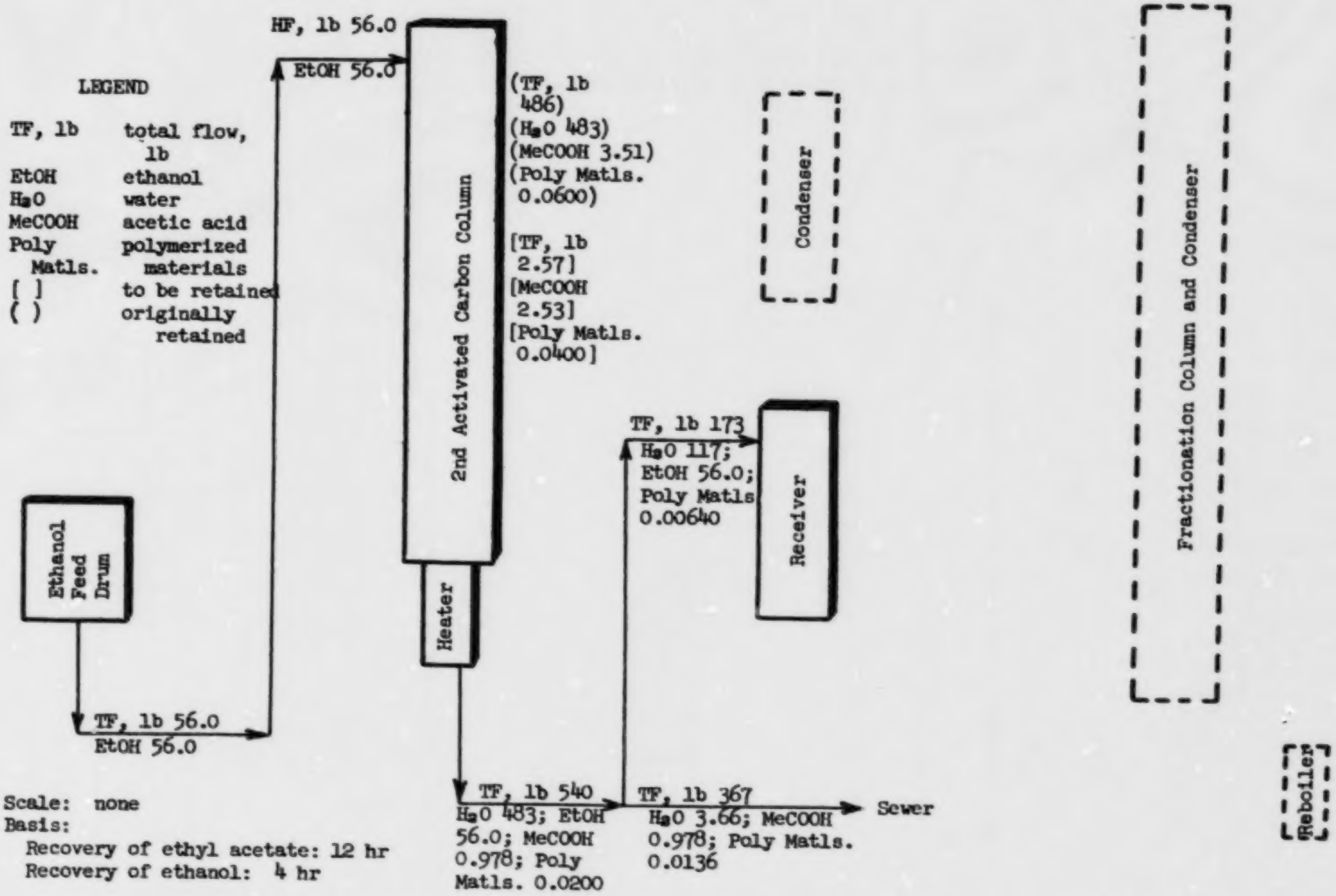
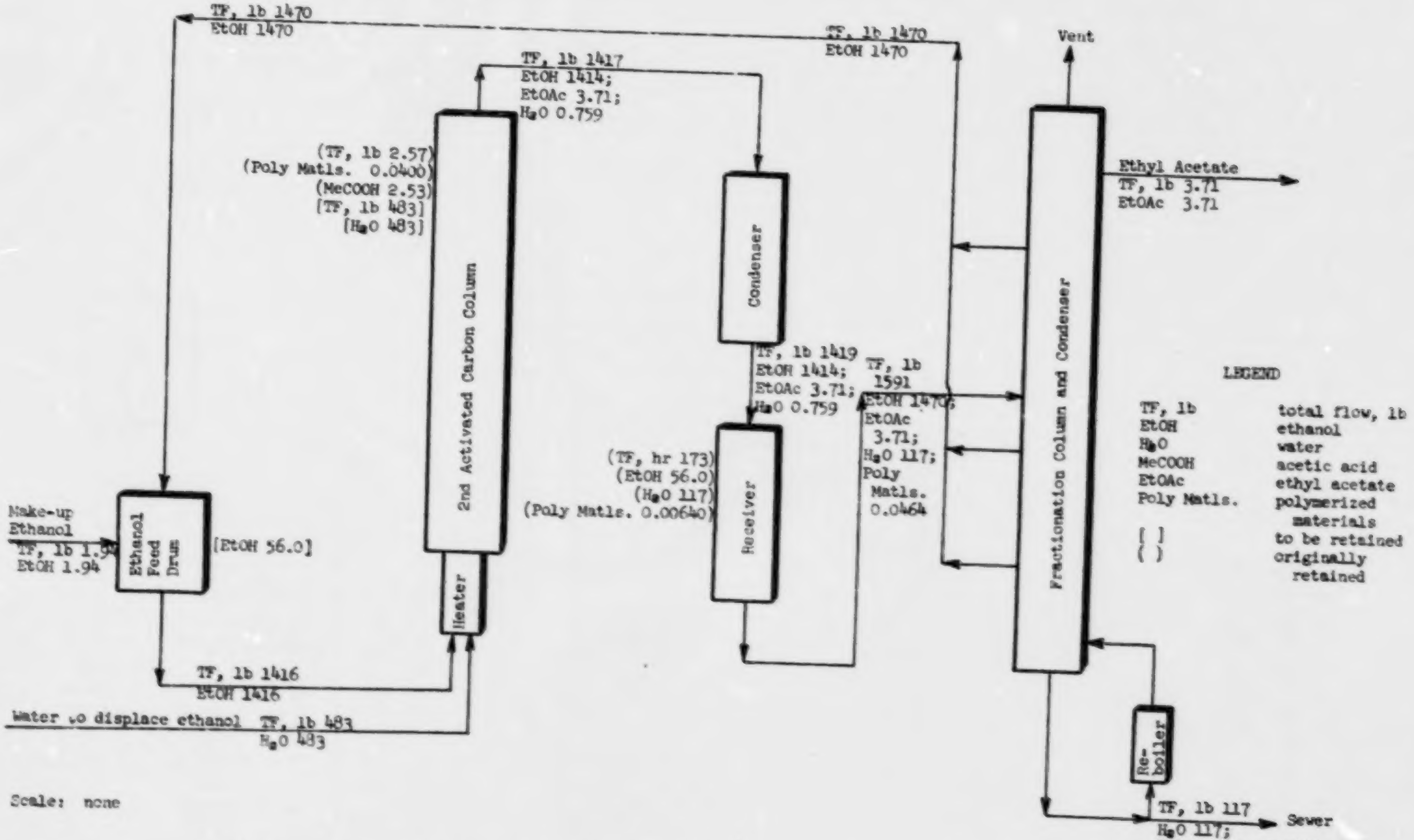

TF, hr 0.639
MeOH 0.639
TF, hr 400
H_2O 400
Vent
Methanol Feed Tank
Vaporizer
1st Activated Carbon Column
(TF, hr 0.639)
(MeOH 0.639)
[TF, hr 92.0]
[H_2O 92.0]
TF, hr
0.639
MeOH
0.639
Condenser
Receiver
TF, hr 309
H_2O 308;
MeOH 0.639
Fractionation Column and Condenser
Water TF, hr 400
H_2O 400
Scale: none
LEGEND
TF, lb total flow
Furf. furfural
MeOH methanol
Poly Matls. Polymerized materials
H_2O water
[ ] to be retained
( ) originally retained
TF, hr 309
H_2O 308;
MeOH 0.639
Feed Tank
Reboiler
TF, hr 308
H_2O 308

Figure 45. Activated carbon regeneration and furfural recovery.
2. Methanol recovery


LEGEND
TF, lb — total flow, lb
EtOH — ethanol
H_2O — water
MeCOOH — acetic acid
Poly Matls. — polymerized materials
[ ] — to be retained
( ) — originally retained
Ethanol Feed Drum
TF, lb 56.0
EtOH 56.0
HF, lb 56.0
EtOH 56.0
2nd Activated Carbon Column
(TF, lb 486)
(H_2O 483)
(MeCOOH 3.51)
(Poly Matls. 0.0600)
[TF, lb 2.57]
[MeCOOH 2.53]
[Poly Matls. 0.0400]
Heater
TF, lb 540
H_2O 483; EtOH 56.0; MeCOOH 0.978; Poly Matls. 0.0200
TF, lb 173
H_2O 117; EtOH 56.0; Poly Matls 0.00640
Receiver
TF, lb 367
H_2O 3.66; MeCOOH 0.978; Poly Matls. 0.0136
Sewer
Condenser
Fractionation Column and Condenser
Reboiler

Scale: none
Basis:
Recovery of ethyl acetate: 12 hr
Recovery of ethanol: 4 hr

Figure 46. Activated carbon regeneration and ethyl acetate recovery.
1. Draining of column


TF, lb 1470
EtOH 1470
TF, lb 1470
EtOH 1470
Vent
TF, lb 1417
EtOH 1414;
EtOAc 3.71;
H_2O 0.759
(TF, lb 2.57)
(Poly Matls. 0.0400)
(MeCOOH 2.53)
[TF, lb 483]
[H_2O 483]
2nd Activated Carbon Column
Heater
Condenser
Receiver
Fractionation Column and Condenser
Ethyl Acetate
TF, lb 3.71
EtOAc 3.71
TF, lb 1419
EtOH 1414;
EtOAc 3.71;
H_2O 0.759
TF, lb
1591
EtOH 1470;
EtOAc
3.71;
H_2O 117;
Poly
Matls.
0.0464
(TF, hr 173)
(EtOH 56.0)
(H_2O 117)
(Poly Matls. 0.00640)
LEGEND
TF, lb total flow, lb
EtOH ethanol
H_2O water
MeCOOH acetic acid
EtOAc ethyl acetate
Poly Matls. polymerized materials
[ ] to be retained
( ) originally retained
Make-up
Ethanol
TF, lb 1.94
EtOH 1.94
Ethanol
Feed
Drum
[EtOH 56.0]
TF, lb 1416
EtOH 1416
Water to displace ethanol TF, lb 483
H_2O 483
Re-
boiler
TF, lb 117
H_2O 117;
Poly Matls. 0.0464
Sewer

Scale: none

Figure 47. Activated carbon regeneration and ethyl acetate recovery.
2. Recovery of ethyl acetate and recovery of ethanol

The individual titles of the figures and the brief calculations are as follows:

I. Fig. 48 — Equipment flow sheet of the separation process.

II. Fig. 49 — Equipment flow sheet of the activated carbon regeneration and furfural recovery.

III. Fig. 50 — Equipment flow sheet of the activated carbon regeneration and ethyl acetate recovery.

IV. Fig. 42 — Overall mass balances — Basis: 50,000 lb (22,700 kg) of evaporator condensate. To combine the separation process and the two recovery-regeneration processes, the flows shown in Fig. 43 are multiplied by 100, those in Fig. 44 and 47 by 1, and those in Fig. 46 and 47 by 33.3.

V. Fig. 43 — Mass flow sheet of the separation process. The quantities indicated on this flow sheet are based on the following calculations:

1. Basis: The total flows shown are based on 500 lb (227 kg) of evaporator condensate feed. It should be noted that three significant figures are used for the flow quantities.
2. Evaporator condensate: The following mean analyses taken from an interim report to sponsors of the project were used.

Acetic acid	1.34	lb (0.61 kg)
Methanol	0.325	lb (0.15 kg)
Furfural	0.0800	lb (0.04 kg)
Total sulfur dioxide	0.490	lb (0.22 kg)
Water	498	lb (226.09 kg)

3. Mass balance around stripping column:
   A. In:
      a. Preheated feed

Acetic acid	1.34	lb (0.61 kg)
Methanol	0.325	lb (0.15 kg)
Furfural	0.0800	lb (0.04 kg)

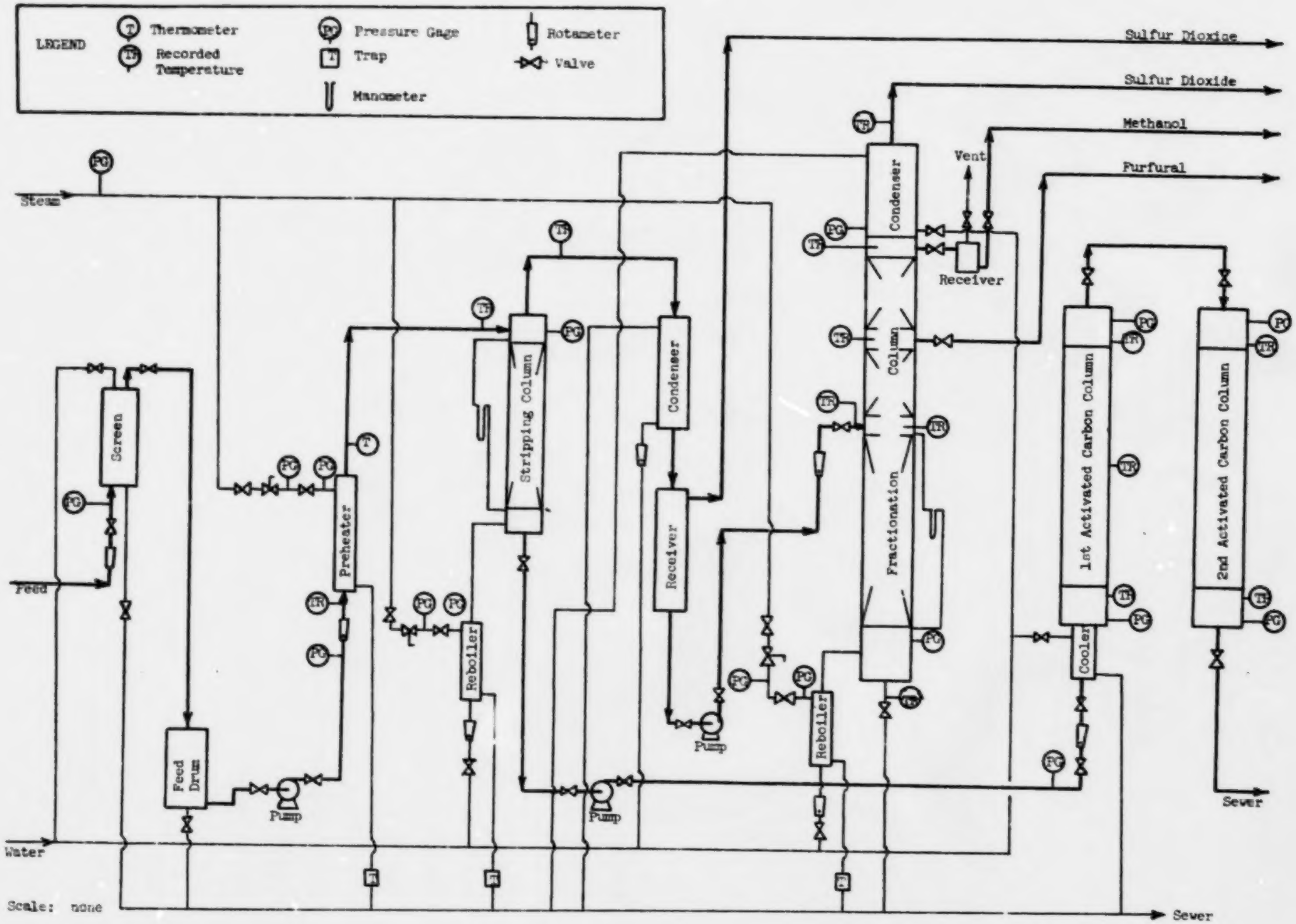

LEGEND
Thermometer
Recorded Temperature
Pressure Gage
Trap
Manometer
Rotameter
Valve
Steam
Feed
Water
Scale: none
Screen
Feed Drum
Pump
Preheater
Reboiler
Stripping Column
Condenser
Receiver
Pump
Condenser
Column
Fractionation
Receiver
Vent
Reboiler
Cooler
1st Activated Carbon Column
2nd Activated Carbon Column
Sulfur Dioxide
Sulfur Dioxide
Methanol
Furfural
Sewer
Sewer
T
TR
PG

Figure 48. Separation process

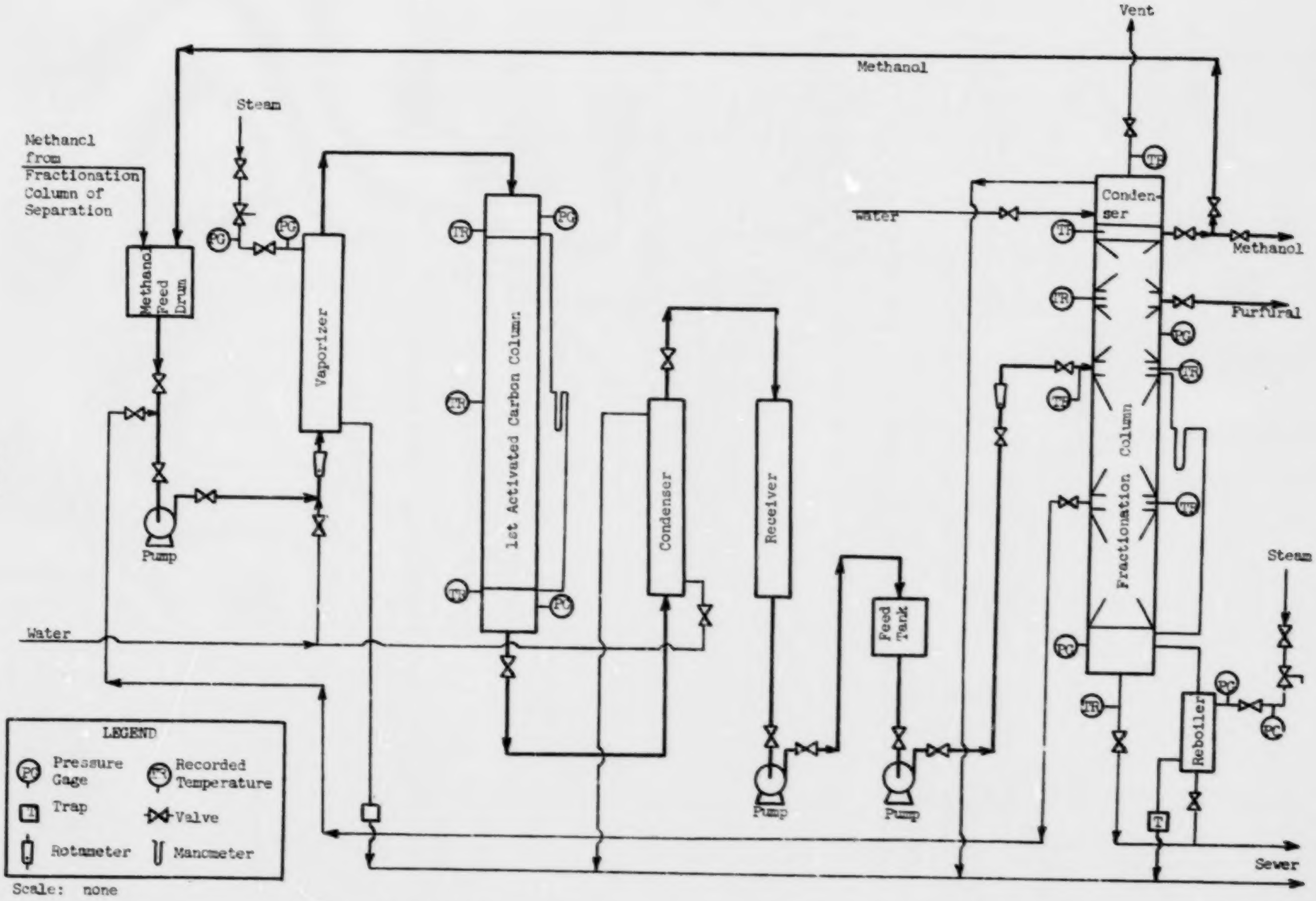
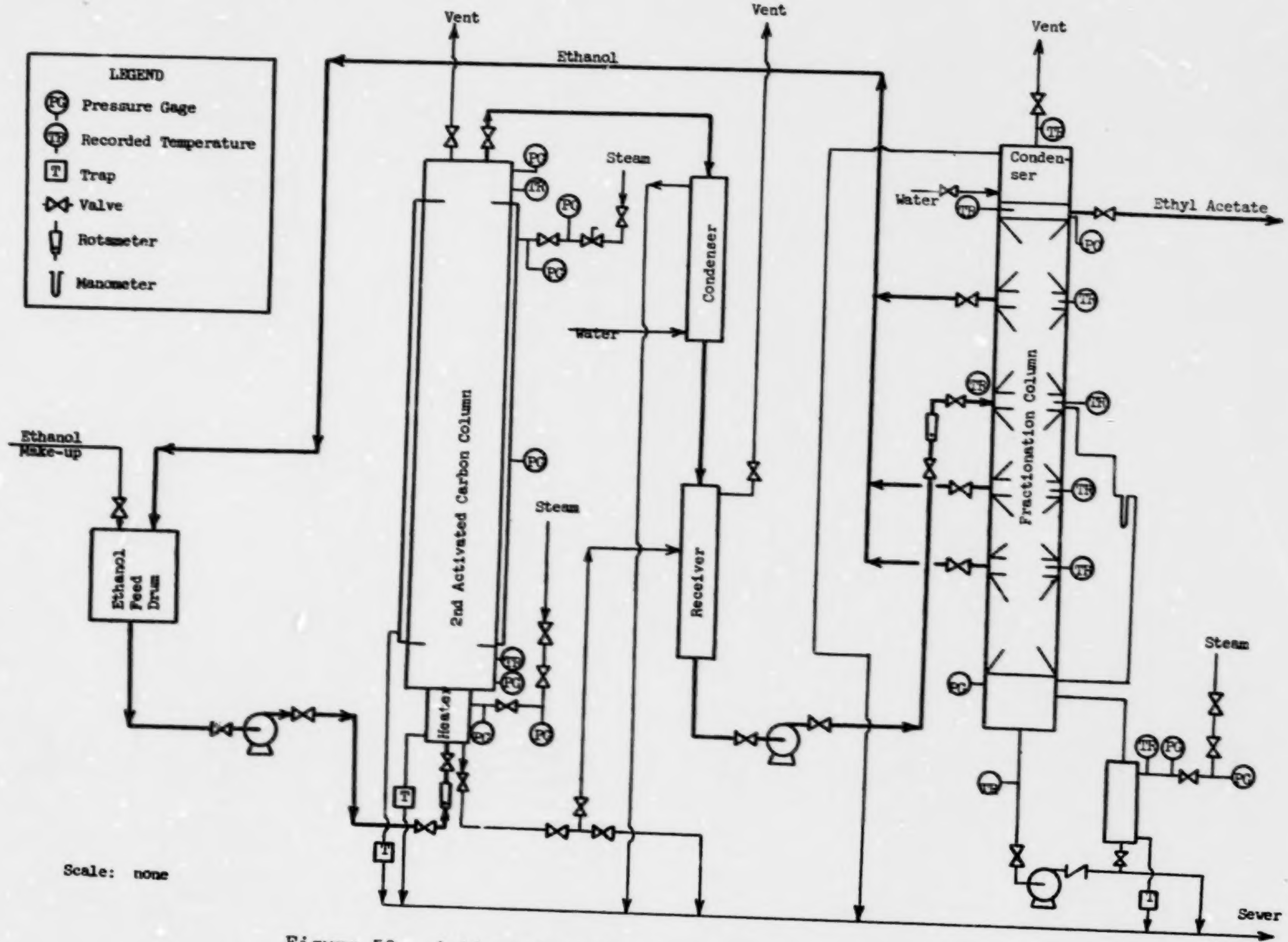

Vent
Methanol
Steam
Methanol from Fractionation Column of Separation
Methanol Feed Drum
PG
PG
Vaporizer
Pump
TR
PG
1st Activated Carbon Column
TR
TR
PG
Condenser
Receiver
Feed Tank
Pump
Pump
Water
Condenser
TR
Methanol
TR
Furfural
PG
TR
TR
Fractionation Column
TR
PC
TR
Steam
PC
Reboiler
PC
T
Water
Sewer
LEGEND
Pressure Gage
Recorded Temperature
Trap
Valve
Rotameter
Manometer
Scale: none

Figure 49. Activated carbon regeneration and furfural recovery


LEGEND
PG Pressure Gage
TR Recorded Temperature
T Trap
Valve
Rotameter
Manometer
Vent
Vent
Vent
Ethanol
Steam
Steam
Steam
Water
Water
Condenser
Receiver
2nd Activated Carbon Column
Heater
Conden-ser
Fractionation Column
Ethyl Acetate
Ethanol Make-up
Ethanol Feed Drum
Sewer
PG
TR
T

Scale: none

Figure 50. Activated carbon regeneration and ethyl acetate recovery

Total sulfur dioxide	0.490	lb	(0.22 kg)
Water	498	lb	(226.09 kg)
	500	lb	(227.00 kg)

b. Steam	30	lb	(13.62 kg)

Total in = 530 lb (240.62 kg).

B. Out:

a. Bottoms — by analysis

Acetic acid	1.17	lb	(0.53 kg)
Methanol	0.160	lb	(0.07 kg)
Furfural	0.040	lb	(0.02 kg)
Total sulfur dioxide	0.0800	lb	(0.04 kg)
Water	499	lb	(226.55 kg)
	500	lb	(227.00 kg)

b. Volatiles — by difference

Acetic acid	0.0560	lb	(0.02 kg)
Methanol	0.165	lb	(0.07 kg)
Furfural	0.0400	lb	(0.02 kg)
Total sulfur dioxide	0.410	lb	(0.19 kg)
Unaccounted acetic acid	0.114	lb	(0.05 kg)
Water	29.2	lb	(13.26 kg)
	30.0	lb	(13.62 kg)

Total out = 530 lb (240.62 kg)

It should be noted that since the compositions of the preheated feed, the gases leaving the receiver, and the fractionation column feed were all based on actual analyses, the "unaccounted acetic acid" has to be used here to complete the acetic acid analysis.

4. Around the fractionation column:

A. In:

a. Feed

Acetic acid	0.0560	lb	(0.02 kg)
Methanol	0.153	lb	(0.07 kg)
Furfural	0.0310	lb	(0.01 kg)
Total sulfur dioxide	0.170	lb	(0.08 kg)

Unaccounted acetic acid	0.114	lb	(0.05 kg)
Water	29.2	lb	(13.26 kg)
	29.7	lb	(13.48 kg)

b. Steam	30.0	lb	(13.62 kg)

Total in = 59.7 lb (27.10 kg)

B. Out

a. SO_2 stream

SO_2	0.135	lb	(0.061 kg)
Methanol	0.003	lb	(0.001 kg)
	0.138	lb	(0.063 kg)

b. Methanol stream

Methanol	0.150	lb	(0.068)
Sulfur dioxide	0.002	lb	(0.001)
	0.152	lb	(0.069)

c. Furfural stream

Furfural	0.0310	lb	(0.014)
Water	0.0020	lb	(0.001)
	0.0330	lb	(0.015)

d. Bottom

Acetic acid	0.0560	lb	(0.025)
Sulfur dioxide	0.0330	lb	(0.015)
Unaccounted HAc	0.114	lb	(0.052)
Water	59.2	lb	(26.877)
	59.4	lb	(26.968)

Total out = 0.138 + 0.152 + 0.0330 + 59.4
= 59.7 lb (27.104 kg)

5. First activated carbon column:

A. In:

Acetic acid	1.17	lb	(0.531 kg)
Methanol	0.160	lb	(0.073 kg)
Furfural	0.0400	lb	(0.018 kg)
Sulfur dioxide	0.0800	lb	(0.036 kg)
Water	499	lb	(226.546 kg)
	500	lb	(227.000 kg)

B. Out:

Acetic acid	1.17 lb	(0.531 kg)
Methanol	0.160 lb	(0.073 kg)
Sulfur dioxide	0.0300 lb	(0.014 kg)
Water	499 lb	(226.546 kg)
	500 lb	(227.000 kg)

C. Retained:

Furfural	0.0400 lb	(0.018 kg)
Sulfur dioxide	0.0500 lb	(0.023 kg)
	0.0900 lb	(0.041 kg)

In = Out + Retained

6. Second activated carbon column:

A. In:

Acetic acid	1.17 lb	(0.531 kg)
Methanol	0.160 lb	(0.073 kg)
Sulfur dioxide	0.0300 lb	(0.014 kg)
Water	499 lb	(226.546 kg)
	500 lb	(227.000 kg)

B. Out:

Methanol	0.160 lb	(0.073 kg)
Sulfur dioxide	0.0100 lb	(0.004 kg)
Water	499 lb	(226.546 kg)
	499 lb	(226.546 kg)

C. Retained:

Acetic acid	1.17 lb	(0.531 kg)
Sulfur dioxide	0.0200 lb	(0.009 kg)
	1.19 lb	(0.540 kg)

In = Out + Retained

VI. Fig. 44 — Activated carbon regeneration and furfural recovery:

1. Furfural recovery.

This flow sheet shows the mass flows during the cycle of furfural recovery. The balances are based on a 16-hour cycle of furfural recovery and an 8-hour cycle of methanol recovery. The flow quantities shown on this sheet are the total flows of 16 hours. The balances of importance are:

A. Around the activated carbon column:

a. In:

Methanol	640 lb	(290.56 kg)
	640 lb	(290.56 kg)

b. Removed from column:

Furfural	4.00 lb	(1.816 kg)
Polymerized materials	4.00 lb	(1.816 kg)
Water	92.0 lb	(41.768 kg)
	100 lb	(45.400 kg)

c. Retained:

Methanol vapor = 0.639 lb (0.290 kg)

calculated as follows:

volume of column = 60 gal. (227.1 l)

number of moles MeOH vapor in the column = $\underline{n}$

compressibility factor $\doteq 1$

$$\therefore \underline{n} = \frac{16.2\,(144)\,(8.02)}{1545\,(607)} = 0.01995 \text{ no. moles}$$

$\therefore$ methanol vapor = 0.639 lb (0.290 kg)

d. Out:

Furfural	4.00 lb	(1.816 kg)
Methanol	639 lb	(290.106 kg)
Polymerized materials	4.00 lb	(1.816 kg)
Water	92.0 lb	(41.768 kg)
	739 lb	(335.506 kg)

640 + 100 = 0.639 + 739

B. Around the fractionation column:

1. In:

Furfural	4.00 lb	(1.816 kg)
Methanol	639 lb	(290.106 kg)
Polymerized materials	4.00 lb	(1.816 kg)
Water	92.0 lb	(41.768 kg)
	739 lb	(335.506 kg)

2. Out:

a. Furfural stream	
Furfural	4.00 lb (1.816 kg)
	4.00 lb (1.816 kg)
b. Bottom	
Polymerized materials	4.00 lb (1.816 kg)
Water	92.0 lb (41.768 kg)
	96.0 lb (43.584 kg)
c. Methanol	
Methanol	639 lb (290.106 kg)
	639 lb (290.106 kg)

739 (335.506 kg) = 4.00 + 96.0 + 639

VII. Fig. 45 — Activated carbon regeneration and furfural recovery:

2. Methanol recovery.

The balances are based on an 8-hour cycle of methanol recovery and the flow quantities shown on this flow sheet are the total flows of 8 hours.

VIII. Fig. 46 — Activated carbon regeneration and ethyl acetate recovery:

1. Draining of column.

IX. Fig. 47 — Activated carbon regeneration and ethyl acetate recovery:

2. Recovery of ethyl acetate and recovery of ethanol.

The balances shown are based on an ethyl acetate recovery cycle of 12 hours and ethanol recovery cycle of 4 hours. The flow quantities shown are totals of 12 hours, except that of the water flow, which is the total of 4 hours.

HEAT BALANCES FOR PILOT PLANT

The balances shown in this section are primarily based on the recorded data shown in the interim report to sponsors of this project and the mass flow quantities in Fig. 42. Since the basic flow quantities in Fig. 42 are 100 times that of Fig. 43, the balances for the separation process made in this section are also 100 times that of the actual flow quantity of 500 lb evaporator condensate processed in 1 hour. The calculations for the regeneration processes are accordingly proportioned.

Since the individual equipment used in the pilot plant is not optimized, and the flow quantities and conditions vary from case to case, it is felt that a total energy balance of the pilot plant would not be helpful in the economy feasibility analyses. Only enthalpy balances are made. The calculations are based on the actual operating conditions, so that estimations of the heat requirements can be made.

Enthalpy balances:

I. Separation process

A. Preheater

		Sp. Heat
Water	49,800 lb (22609.2 kg)	1.05
Furfural	8.08 lb (3.6 kg)	0.418
Methanol	32.5 lb (14.8 kg)	0.66
Acetic acid	134 lb (60.8 kg)	0.54
Sulfur dioxide	49.0 lb (22.2 kg)	0.5 (estimated)

The above heated from 134°F (56.7°C) to 212°F (100.0°C)

Heat required, $H_1 = [49800\ (1.05) + 8.00\ (0.418) + 32.5\ (0.66) + 134\ (0.54) + 49.0\ (0.5)]\ (212-134) = 4{,}090{,}000$ Btu (1,030,680 kg-cal).

B. Stripping column reboiler

To heat 3000 lb (1362 kg) of water from 70°F (21.1°C) to 247°F (119.4°C) vapor, heat required $H_2 = 3000\ [(247-212)\ (0.482) + 970 + (212-70)] = 3{,}390{,}000$ Btu (854,280 kg-cal).

Estimated amount of heat required by the stripping column:

1. Assume there is no heat loss from the point the condensate leaves the preheater to the feed point. The feed is in the liquid state and at a temperature which is just about the bubble point. Therefore, no heat is required to bring the feed up to the bubble point.

2. Heat of vaporization = 2920 (970.3) + 4.00 (107.5) (1.8) + 16.5 (262.8) (1.8) + 41.0 (94.9) (1.8) + 5.60 (96.8) (1.8) + 11.4 (300) (1.8) = 2,860,000 Btu (720,720 kg-cal).

3. The bottom stream leaves at 210°F (98.9°C). Heat given up by the bottom stream = [(49900 + x) (1) + 4.00 (0.418) + 16.0 (0.566) + 8.00 (0.5) + 117 (0.487)] (212-210) = 99,900 + 2*x*.

   If 73 psig (51.3 kg/cm^2) live stream is used: 2,860,000 - (99,900 + 2*x*) = [(318-212) (0.482) + 970.3 + (212-210)] x
   1025x = 2,959,900
   x = 2690 lb (1221.3 kg)

   Total heat required = 2,750,000 Btu (693,000 kg-cal). This compares with 3,390,000 Btu (854,280 kg-cal).

C. Stripping column condenser

C_p of the components at gaseous state

Water vapor	0.482	Btu/lb/°F (0.482 kg-cal/kg/°C)
Methanol	0.458	Btu/lb/°F (0.458 kg-cal/kg/°C)
Sulfur dioxide	0.134	Btu/lb/°F (0.134 kg-cal/kg/°C)
Acetic acid	1.50	Btu/lb/°F (1.50 kg-cal/kg/°C)
Furfural	0.6	Btu/lb/°F (0.6 kg-cal/kg/°C) (estimated).

C_p of components at liquid state

Water	1 Btu/lb/°F (1 kg-cal/kg/°C)
Sulfur dioxide	0.5 (estimated)
Methanol	0.566
Acetic acid	0.487
Furfural	0.418
Unaccounted HAc	0.5 (estimated)

Heats of vaporization of components

Water	970.3 Btu/lb	(539.0 kg-cal/kg)
Acetic acid	96.8 cal/g (*ca*)	(174.2 Btu/lb)
Methanol	262.8 cal/g (*ca*)	(473.0 Btu/lb)
Furfural	107.5 cal/g (*ca*)	(193.5 Btu/lb)
Sulfur dioxide	94.9 cal/g (*ca*)	(170.8 Btu/lb)

1. Those gases cooled from 213°F (100.6°C) to 203°F (95.0°C) without condensing

Water vapor	3.90	lb (1.771 kg)
Sulfur dioxide	24.0	lb (10.896 kg)
Methanol	1.20	lb (0.545 kg)
Furfural	0.900	lb (0.409 kg)

H_3 = [3.90 (0.482) + 24.0 (0.134) + 1.20 (0.458) + 0.900 (0.6)] (10) = 61.9 Btu (15.6 kg-cal).

2. Those gases cooled from 213°F (100.6°C) to 212°F (100°C), condensed, and cooled to 203°F (95°C)

Water	2,920	lb (1325.7 kg)
Sulfur dioxide	17.0	lb (7.7 kg)
Methanol	15.3	lb (6.9 kg)
Furfural	3.10	lb (1.4 kg)
Acetic acid	5.60	lb (2.5 kg)
Unaccounted HAc	11.4	lb (5.2 kg)

H_{41} = [2920 (0.482) + 17.0 (0.134) + 15.0 (0.458) + 3.10 (0.6) + 5.60 (1.5) + 11.4 (1)] (1) = 1440 Btu (362.9 kg-cal).

It should be mentioned that the sulfur compounds that condensed into liquid form are taken as SO_2 and that the C_p of the unaccounted acetic acid is estimated as 1.

H_{42} = 2920 (970) + 17.0 (94.9) (1.8) + 15.3 (263) (1.8) + 3.10 (108) (1.8) + 5.60 (96.8) (1.8) + 11.4 (100) (1.8) = 2,850,000 Btu (718,200 kg-cal).

The sulfur compounds are taken as SO_2 and the λ of the unaccounted acetic acid is estimated as 100 cal/g (180 Btu/16)

H_{43} = [2920 (1) + 17.0 (0.5) + 15.3 (0.566) + 3.10 (0.418) + 5.60 (0.487) + 11.4 (0.5)] (212-203) = 26,500 Btu (6678 kg-cal)

$H_4 = H_{41} + H_{42} + H_{43}$ = 2,880,000 Btu (725,760 kg-cal).

D. Fractionation column

1. Reboiler — evaporates 3000 lb (1362 kg) of water from 70°F (21.1°C) to 247°F vapor. Heat required = [(212-50) + 970 + 0.482 (35)] (3000) = 3,390,000 Btu (854,280 kg-cal). Estimated amount of heat required by the fractionation column:
    a. Heat to bring the feed temperature, 166°F (74.4°C) to its bubble point, say 205°F (96.1°C) = [2920 (1) + 3.10 (0.418) + 15.3 (0.566) + 17.0 (0.5) + 5.60 (0.478) + 11.4 (0.5)] (205-166) = 115,000 Btu (28,980 gm-cal)
    b. Heat of vaporization = (15.0 + 0.3) (262.8) (1.8) + (0.2 + 13.5) (94.9) (1.8) + 0.2 (970) + 3.10 (107.5) (1.8) = 10,300 Btu (2596 gm-cal)
    c. Heat to bring the bottom stream [(x + 2920 - 0.2) lb of water, 3.30 SO_2, 5.60 HAc and 11.4 unaccounted HAc] from 205°F (96.1°C) to 210°F (98.9°C) = [(2920 + x) (1) + 3.30 (0.5) + 5.60 (0.487) + 11.4 (0.5)] (210-205) = 5(2930 + x) = 14650 + 5x (x = lb of steam used).

       If live steam is used, and the steam comes in at 73 psig (5.13 kg/cm^2) (318°F) (158.9°C) and leaves at 210°F (98.9°C) as liquid, then 115000 + 10300 + 14650 + 5x [(318-212) (0.482) + 970.3 x + (212-210)] x.
       x = 137 lb (62.2 kg)
       Total heat required = 141,000 Btu (35532 kg-cal). This compares with the heat required for the reboiler, 3,390,000 Btu (854280 kg-cal).
2. Let 149°F (65°C) be the reference temperature. Heat in with steam which is at 213°F (100.6°C), H_1 = 3000 [(0.482) (1) + 970 + (1) (63)] = 3,100,000 Btu (781200 kg-cal).
3. Heat in with the feed which contains:

Water	2920	lb (1325.7 kg)
Furfural	3.10	lb (1.4 kg)

Methanol	15.3	lb (6.9 kg)
Sulfur dioxide	17.0	lb (7.7 kg)
Acetic acid	5.60	lb (2.5 kg)
Unaccounted HAc	11.4	lb (5.2 kg)

H_2 [2920 (1) + 3.10 (0.418) + 15.3 (0.566) + 17.0 (0.5) + 5.60 (0.487) + 11.4 (0.5)] (166-149) = 50,100 Btu (12625 kg-cal).

4. Heat out with methanol, $H_3 = 0$.
5. Heat out with furfural stream:

   H_4 = [3.10 (0.418) + 0.200 (1)] (213-149) = 96.0 Btu (24.2 kg-cal).
6. Heat out with the bottom stream:

   H_5 = [5920 (1) + 3.30 (0.5) + 5.60 (0.487) + 11.4 (0.5)] (210-149) = 36,200 Btu (9122.4 kg-cal).
7. Heat out with sulfur dioxide stream, $H_6 = 0$.
8. Neglect the heat of solution and heat of dilution.
9. Heat loss of the column, H_7.

   3,100,000 + 50,100 = 96 + 36,200 + H_7.

   Heat loss = 3,110,000 Btu (783720 kg-cal).

E. Cooler before the first carbon column. The stripping column bottom is 50,000 lb (22700 kg) containing:

Furfural	4.00	lb (1.82 kg)
Methanol	16.0	lb (7.26 kg)
Sulfur dioxide	8.00	lb (3.63 kg)
Acetic acid	117	lb (53.12 kg)
Water	49900	lb (22654.6 kg).

To cool this stream from 212°F (100°C) to 140°F (60°C), the heat required = [4.00 (0.418) + 16.0 (0.566) + 8.00 (0.5) + 117 (0.487) + 49900 (1)] (212-140) = 3,600,000 Btu (907200 kg-cal).

F. Condenser after fractionation column.

The SO_2 gas stream comes in at 149°F (65°C) and leaves at 97°F (36.1°C).

Heat given up = [13.5 (0.134) + 0.300 (0.458)] (149-97) = 101 Btu (25.4 kg-cal).

Heat given up by the methanol stream during condensing from vapor to liquid = 15.0 (263) (1.8) + 0.2 (94.9) (1.8) = 7140 Btu (1799.3 kg-cal).

Total heat removed by cooling water = 7240 Btu (1824.5 kg-cal).

II. Recovery of furfural and methanol

A. Furfural recovery

1. Vaporizer

Assume methanol available at 70°F (21.1°C) from feed tank.

sp. gr. = 0.792

C_p = 0.6 (liquid)

C_p = 0.458 (vapor)

λ = 262.8 cal/g

b.p. = 64.7°C = 148.5°F

a. Heat required to heat the MeOH from 7C°F (21.1°C) to 148.5°F (64.7°C). H_1 = 640 (148.5-70) (0.6) = 30,100 Btu (7585.2 kg-cal).

b. Heat required to heat the vapor from 148.5°F (67.7°C) to 151°F (66.1°C). H_3 = 640 (0.458) (1.8) (2.5) = 1320 Btu (332.6 kg-cal).

2. Condenser after the activated carbon column.

The liquid coming out of the activated carbon column contains 639 lb (290.1 kg) of methanol, 92.0 lb (41.8 kg) of water, 4.00 lb (1.8 kg) of furfural, and 4.00 lb (1.8 kg) of polymerized materials. The temperature is at 148°F (64.4°C). After the condenser, it is cooled to an average temperature of 100°F (37.8°C). Heat given up = (148-100) [639 (0.566) + 92.0 (1) + 4.00 (0.418) + 4.0 (0.5)] = 22,000 Btu (5544 kg-cal).

3. Fractionation column

a. Reboiler

Assume that the liquid comes in at 210°F (98.9°C) and goes out at 247°F (119.4°C) (same as the other reboilers in "separation process"), and that 9.60 lb (4.36 kg) of the liquid are reboiled. In 9.60 lb (4.36 kg) of the bottom liquid there are 9.20 lb (4.17 kg) of water and 0.400 lb (0.18 kg) of polymerized materials.

Make the following assumptions for the polymerized materials:

C_p (liquid)	0.6
C_p (vapor)	0.3
λ	300 cal/g (540 Btu/lb)
b.p.	212°F (100°C)

Heat required to heat liquid from 210°F (98.9°C) to 212°F (100°C) = 9.20 (1) (2) + 0.400 (0.6) (2) = 18.9 Btu (4.76 kg-cal)

Heat of vaporization = 9.20 (970.3) + 0.400 (300) (1.8) = 9140 Btu (2303 kg-cal)

Heat required to heat the vapor from 212°F (100°C) to 247°F (119.4°C) = 35 [9.20 (0.482) + 0.400 (0.3)] = 159 Btu (40 kg-cal)

Total heat required = 9320 Btu (2348.6 kg-cal)

b. Use of 149°F (65°C) as reference temperature.

Heat in = [9.20 (0.482) + 0.400 (0.3)] (213-212) + 9.20 (970.3) + 0.400 (300) (1.8) + [9.20 (1) + 0.400 (0.6)] (212-149) = 9740 Btu (2454.5 kg-cal)

Heat out = [101(1) + 4.40 (0.6)] (213-149) = 6630 Btu (1670.8 kg-cal)

Heat loss = 3110 Btu (783.7 kg-cal)

It can be seen that the heat loss is based on several assumptions. The actual loss can be either higher or lower.

4. Fractionation column condenser.

No flow quantity of the vent is available. Heat given up by the methanol = 639 (263) (1.8) = 302,000 Btu (76,104 kg-cal).

B. Methanol recovery

Assume same operating conditions on the fractionation column.

Enthalpy balance around the fractionation column:

1. Reboiler

Assume 30.8 lb (13.98 kg) of reboiling. Heat required to heat the liquid (which is essentially water) from 210°F (98.9°C) to 212°F (100°C) = 30.8 (1) (2) = 61.6 Btu (15.5 kg-cal)

Heat of evaporation = 30.8 (970.3) = 29900 Btu (7534.8 kg-cal)

Heat required to heat vapor from 212°F (100°C) to 247°F (119.4°C) = 35 (30.8) (0.482) = 520 Btu (131 kg-cal)

Total heat required = 30,500 Btu (7686 kg-cal)

2. Condenser after fractionation column.

No vent flow quantity is available. Heat given up by methanol = 0.639 (263) (1.8) = 302 Btu (76.1 kg-cal)

3. Heat loss — fractionation column.

Use 149°F (65°C) as reference temperature.

Heat in = 30.8 [(0.482) (1) + 970.3 + (1) (63)] = 31,800 Btu.

Heat out = (308-30.8) (1) (64) = 21,700 Btu (5468.4 kg-cal).

Heat loss = 10,100 Btu (2545.2 kg-cal).

The heat loss shown here can be either higher or lower for similar reasons as indicated before.

III. Recovery of ethyl acetate and ethanol

A. Ethyl acetate recovery

For ethanol:

$\rho = 0.785$

b.p. = 78.5°C = 173.3°F

This is the exit temperature of the ethanol vapor. Since the heater is attached to the activated carbon column, this is also the inlet ethanol vapor temperature to the column.

λ = 204 cal/g

C_p = 0.406 cal/g/°C (0.406 Btu/lb/°F) (vapor)

C_p = 0.456 cal/g°C (0.456 Btu/lb/°F) (liquid)

For acetic acid

λ = 96.8 cal/g (174.2 Btu/lb)

C_p = 1.50 cal/g/°C (1.50 Btu/lb/°F) (vapor)

C_p = 0.468 cal/g/°C (0.468 Btu/lb/°F) (liquid)

For ethyl acetate

λ = 102 cal/g (183.6 Btu/lb)

C_p = 0.371 cal/g/°C (0.371 Btu/lb./°F) (vapor)

C_p = 0.459 cal/g/°C (0.459 Btu/lb/°F) (liquid)

1. Heater before the activated carbon column.

   Ethanol flow = $1416 \frac{1.17}{3.51} (100)$ = 47,200 lb (21428.8 kg)

   Assume at 70°F (21.1°C)

   Heat required = 47,200 [0.456 (173-70) + 204 (1.8)] = 19,500,000 Btu (4914000 kg-cal).
2. No information for the steam consumption in the steam jacket is available. It is believed that unless some unusual source of high heat loss exists, the steam requirement for this item should not be high.
3. Heat of reaction

   $CH_3COOH(g) + C_2H_5OH(g) \rightarrow CH_3COOC_2H_5(g) + H_2O(g)$

   Assuming constant pressure and volume, the heat of reaction is estimated as follows:

   ΔH_c of $CH_3COOH(g)$ = -219.82 K cal/g-mole

   ΔH_c of $C_2H_5OH(g)$ = -336.82 K cal/g-mole

   ΔH_c of $CH_3COOC_2H_5(g)$ = -547.46 K cal/g-mole.

These are the standard heat of combustion with reference conditions of 25°C (77°F), 1 atm. pressure and gaseous substances in ideal state.

∴ Total heat of reaction = $\frac{-12700\ (124)\ (454)}{88\ (252)}$ = -32,400 Btu (-8164.8 kg-cal).

Since the major final products are gaseous carbon dioxide and liquid water, it is necessary in this case to deduct the latent heat of vaporization of the liquid water formed.

Latent heat = $\frac{124}{88}$ (18) (994) = 25,200 Btu (6350.4 kg-cal)

∴ The net heat of reaction = -7200 Btu (-1814.4 kg-cal).

4. Fractionation column

   a. Reboiler

      Assume 390 lb (177.1 kg) reboiling. Heat required to heat the liquid which is essentially water from 210°F (98.9°C) to 247°F (119.4°C) = 390 (1) (2) = 780 Btu (196.6 kg-cal).

      Heat of evaporation = 390 (970.3) = 378,000 Btu (9526 kg-cal).

      Heat required to heat the vapor from 212°F (100°C) to 247°F (119.4°C) = 390, (0.482) (35) = 6580 Btu (1658.2 kg-cal).

      Total heat required = 385,000 Btu (97020 kg-cal).

   b. Heat loss around column.

      Use 157°F (69.4°C) as reference temperature.

      Heat in:

      Heat in with feed = (174-157) [49000 (0.456) + 3900 (1) + 124 (0.459)] = 447,000 Btu (112644 kg-cal).

      Heat in with reboiled liquid = 390 [(0.482) (1) + 970.3 + 1 (213-157)] = 400,000 Btu (100800 kg-cal).

      Total in = 847,000 Btu (213444 kg-cal).

      Heat out with ethanol = (168-157) (49,000) (0.456) = 246,000 Btu (61992 kg-cal).

      Heat out with bottom liquid = (3900 + 390) (213-157) (1) = 240,000 Btu (60480 kg-cal).

Total heat out = 486,000 Btu (122472 kg-cal).

Heat loss = 361,000 Btu (90972 kg-cal).

It should be noted again that the heat loss shown here could be either higher or lower depending upon the operating conditions.

5. Condenser after fractionation column. No vent flow quantity is available. Heat to be given up in condensing the ethyl acetate = 124 (102) (1.8) = 22,800 Btu (5745.6 kg-cal).

Summary of Heat Balances

I. Basis: To process 50,000 lb (22700 kg) of evaporator condensate in the pilot at the Appleton Division Mill of Consolidated Papers, Inc.

II. Calculations are based on the actual operating conditions of the pilot plant. It should be noted that:
   - A. The individual pieces of equipment are not optimized; and
   - B. The process may or may not be exactly suitable for the particular evaporator condensate.

III. Heat Required
   - A. Separation Process
      - 1. Preheater 4,090,000 Btu (1030680 kg-cal)
      - 2. Stripping Column 3,390,000[a] Btu (854280 kg-cal)
      - 3. Fractionation Column 3,390,000[b] Btu (854280 kg-cal)
   - B. Recovery of Furfural and Methanol
      - 1. Furfural Recovery
         - a. Vaporizer 346,000 Btu (87192 kg-cal)
         - b. Fractionation Column 9,140 Btu (2303.3 kg-cal)
      - 2. Methanol Recovery
         - a. Fractionation Column 30,500 Btu (7686 kg-cal)

---

[a] These are based on the actual steam consumptions. This indirect heating may or may not be desirable in large scale practical operation. If live steam is used, this quantity could be reduced to 2,750,000 Btu. (693,000 kg-cal).

[b] Similar to a. This could be reduced to 141,000 Btu. (35,532 kg-cal).

C. Recovery of Ethyl Acetate and Ethanol

1. Heater 19,500,000[c] Btu (4914000 kg-cal)
2. Fractionation Column 385,000 Btu (97020 kg-cal)
3. Heat of Reaction -7,200 Btu (-1814.4 kg-cal)

Total heat consumption = 31,100,000[d] Btu (7837200 kg-cal).

IV. Heat Removed

A. Separation Process
1. Stripping Column Condenser 2,880,000 Btu (725760 kg-cal)
2. First Carbon Column Cooler 3,600,000 Btu (907200 kg-cal)
3. Fractionation Column Condenser 7,240 Btu (1824.5 kg-cal)

B. Recovery of Furfural and Methanol
1. Furfural Recovery
    a. Fractionation Column Condenser 302,000 Btu (76104 kg-cal)
2. Methanol Recovery
    a. Fractionation Column Condenser 302 Btu (76.1 kg-cal)

C. Recovery of Ethyl Acetate and Ethanol
1. Fractionation Column Condenser 22,800 Btu (5745.6 kg-cal)

Total heat removed = 6,810,000 Btu (1716120 kg-cal).

COST ESTIMATE

With a basis of calculation of 50,000 (22,700 kg) pounds of the Appleton Division mill of Consolidated Papers, Inc. condensate, the value of the products potentially recoverable and the economic benefit from the removal of 200 (90.8 kg) pounds of BOD_5 gave the following summary of values to be derived from the process shown in Table 17. It should be mentioned that no credit has been given to the value of the reusable water or recovered sulfite liquor.

---

[c] This figure is known to be too high due to inefficient pilot plant operating conditions. According to the latest revised arrangement and operating conditions the steam consumption for this item should be 4,000,000 Btu. (1008000 kg-cal)

[d] The revised total heat required = 11,700,000 Btu. (2948400 kg-cal)

The major operating expense is steam, and with an estimated power consumption and labor requirement for an automated system, the combined expense and estimated gross net income per year are shown in the same table.

These figures provide guidance as to which portions of the process are most productive of byproducts and which might be simplified, modified, or eliminated with little detriment to the overall economic performance of the installation. Such modifications and more accurate data on costs of operation would have to be provided by detailed full-scale design work specific to the desires of the local mill management.

POLLUTIONAL BALANCES

To show the effect of recovering the various chemicals from the condensates, upon the pollution load, the BOD_5 values of these materials have been calculated and assembled as a balance sheet. This is given in Table 18. The relative BOD_5 values of these materials have been taken from tables previously published in Sewage and Industrial Wastes. Of the 202 pounds (91.7 kg) of BOD_5 admitted into the system (by analyses), 161 pounds (73.1 kg) have been accounted for by using equivalent BOD_5 values of these materials.

CONCLUSIONS

Based on the analysis of the recovered materials and the operating data, the conclusion can be drawn that the process is economically feasible. Sizing of the equipment and more accurate economic feasibility analysis were intended but not made because of these facts:

Table 17. RECOVERABLE VALUES BASED ON THE CONDENSATE OF CONSOLIDATED PAPERS, INC.

I. Basis: To process 50,000 (22,700 kg) pounds of the evaporator condensate of the Appleton Division Mill, Consolidated Papers, Inc.

II. Recoverable Values[a]	
1. Products	
7.10 lb (3.22 kg) of furfural, 12¢/lb (26.4¢/kg)	$ 0.85
15.2 lb (6.9 kg) of methanol, 10¢/gal. (22.0¢/kg)	0.23
127.0 lb (57.6 kg) of ethyl acetate, 9¢/lb (19.8¢/kg)	11.43
43.6 lb (19.8 kg) of SO_2, 0.1¢/lb (0.22¢/kg)	0.04
	$12.55
2. Savings on BOD$_5$ reduction	
203 lb (92.9 kg) BOD$_5$, 4¢/lb (8.8¢/kg)	$ 8.06
Total	$20.61
III. Estimated Operating Costs	
1. Steam	
11,700 lb (5311.8 kg), $1.00/1000 lb ($2.20/1000 kg)	$11.70
2. Power	
Assumptions:	
Capacity = 100,000 lb (45400 kg) of evaporator condensate/hour Pumps = 100 hp Power cost = 1¢/kw-hr	$ 0.38
3. Labor	
Assumptions:	
Number of operators = 1 operator/8-hr shift Wage = $10,000/annum Days operated per year = 350 Other assumptions = same as under Power cost Labor cost	$ 1.59
4. Ethanol	
64.7 lb (29.4 kg), 9¢/lb (19.8¢/kg)	$ 5.83
Total	$19.50

IV. Estimated Gross Income per Annum = (20.61 - 19.50) (2) (24) (350) = $18,600

This net income is based on a plant capacity of 100,000 lb (45400 kg) of condensate per hour

---

[a] No credit has been given to the value of the reusable water or the recovered sulfite liquor.

Table 18. POLLUTIONAL BALANCE SHEET

	MeOH[a]		Acetic Acid[b]		SO$_2$[c]		Furfural[d]		BOD$_5$-lb(kg)	
	lb(kg)	BOD$_5$-lb(kg)	lb(kg)	BOD$_5$-lb(kg)	lb(kg)	BOD$_5$-lb(kg)	lb(kg)	BOD$_5$-lb(kg)	In	Out
Into system	32.5 (14.8)	27.95 (12.69)	134.0 (60.83)	100.50 (45.63)	49.0 (22.25)	12.25 (5.56)	8.0 (3.63)	6.16 (2.80)	146.86 (66.67)	
Recovery										
Separation										
SO$_2$ stream	1.50 (0.68)	1.29 (0.58)	0 (0)	0 (0)	37.5 (17.02)	9.38 (4.26)	0.9 (0.41)	0.69 (0.31)		11.36 (5.16)
MeOH stream	15.0 (6.81)	12.9 (5.86)	0 (0)	0 (0)	0.2 (0.09)	0.05 (0.02)	0 (0)	0 (0)		12.95 (5.88)
Furfural stream	0.0 (0.0)	0.0 (0.0)	0 (0)	0 (0)	0 (0)	0 (0)	3.1 (1.41)	2.39 (1.08)		2.39 (1.08)
Regeneration										
Furfural column	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	4.0 (1.82)	3.08 (1.40)		3.08 (1.40)
Acetic acid column	0 (0)	0 (0)	123.7[e] (56.15)	63.25[f] (28.72)	0 (0)	0 (0)	0 (0)	0 (0)		63.25 (28.71)
										93.03 (42.24)
Re-usable water stream	16.0 (7.26)	13.76 (6.25)	0 (0)	0 (0)	2.0 (0.91)	0.5 (0.23)	0 (0)	0 (0)		14.26 (6.47)
										14.26 (6.47)
Waste material to be burned										
From separation	0 (0)	0 (0)	5.60 (2.54)	4.20 (1.91)	0 (0)	0 (0)	0 (0)	0 (0)		4.20 (1.91)
Unaccounted acetic acid	0 (0)	0 (0)	11.50 (5.22)	8.55 (3.88)	0 (0)	0 (0)	0 (0)	0 (0)		8.55 (3.88)
From furfural regeneration	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)		0.00 (0.00)
From acetic acid regeneration	0 (0)	0 (0)	32.6 (14.80)	24.45 (11.10)	0 (0)	0 (0)	0 (0)	0 (0)		24.45 (11.10)
										37.20 (16.89)
Total									146.86 (66.67)	144.49 (65.60)

Total BOD$_5$ into system (by analyses) based on mean data of Report Two, page 7, 202.3 lb (91.84 kg)
Total BOD$_5$ into system based on calculated data, 146.86 lb (66.67 kg)
BOD$_5$ in re-usable water, 14.26 lb (6.47 kg)
BOD$_5$ removal – based on 202.3 lb (91.84 kg) into system, 93.0%
BOD$_5$ removal – based on 146.86 lb (66.67 kg) into system, 90.3%

Difference in calculated and analyzed BOD$_5$ into system largely due to carbohydrates which would be burned with waste material.

---

[a] 0.86 lb BOD$_5$/lb MeOH – Sewage Ind. Wastes 27(9):1044 (Sept., 1955):

[b] 0.75 lb BOD$_5$/lb acetic acid – Sewage Ind. Wastes 30(5):677 (May, 1958).

[c] 0.25 lb BOD$_5$/lb SO$_2$ – not a true BOD$_5$ but included as BOD$_5$.

[d] 0.77 lb BOD$_5$/lb furfural – Sewage Ind. Wastes 27(9):1046 (Sept., 1955).

[e] As ethyl acetate.

[f] Calculated from equivalent acetic acid.

The general process for which pilot data were available was not specifically designed for processing the evaporator condensate at the Appleton Division Mill of Consolidated Papers, Inc.;

The individual pieces of equipment were mostly not optimized;

The chemical constituents and physical conditions of the evaporator condensates from different effects of the evaporating systems at different mills would be different; and

The flow quantities would vary from case to case.

It is felt that to avoid misleading the reader, the design of full-scale equipment, calculation of energy balance, cost estimation and the complete economic analysis should be done for the individual mills. Based upon the mass and heat balances done, the following points have caught our attention:

1. The use of direct steam instead of a reboiler for the stripping column would save some heat and capital expense.
2. More saving if direct steam is used for the fractionation column.
3. The elimination of the condenser after the first activated carbon column in the furfural recovery process would be logical from both capital and operating cost standpoints.
4. The elimination of the condenser after the second activated carbon column would be reasonable. A vapor feed to the fractionation column could work out well.

SECTION VII

LOW TEMPERATURE REGENERATION OF CARBON

METHODOLOGY

This phase of the project has to do with an attempt to scale up prior laboratory development studies for low temperature [(200°C) (392°F)] regeneration of carbon adsorption columns. Previous projects performed at The Institute of Paper Chemistry in which removal of BOD_5 and COD contributing materials from the condensates derived from the evaporation of spent sulfite liquors were studied utilized 2-inch (5.08 cm) glass and stainless steel columns. Successful regeneration of this carbon over 32 cycles by applying heat to the column by means of an electric tape and superheated steam lead to its inclusion in this project. It was obvious that another system for heating of the larger column would have to be found, and without the introduction of additional water which would result in diluting the concentrated materials.

Early in 1971 it had been learned that Messrs. Bela M. Fabuss and Wilson C. Dubois of Lowell Technological Institute had applied for a patent entitled "Apparatus and Process for Desorption of Filter Beds by Electric Current." Basically, the process consists of utilizing the carbon bed itself as an electrical resistance heater, permitting a rapid temperature rise without any indirect heat transfer. Contacts with Professor Fabuss eventually lead to an agreement with Lowell Technological Institute to construct an activated carbon column incorporating this means of heat regeneration. Operation of this unit is the subject of this phase of the project.

The unit as constructed by Lowell consisted of a one-foot (30.5 cm) diameter stainless steel column with a total height of 5 feet (1.52 m) and containing 4 feet (1.22 m) of activated carbon. Stainless steel grid electrodes 1/2 inch (1.27 cm) thick were spaced at 1-foot (30.48 cm) intervals. A stainless steel screen was fastened to the underside of the bottom electrode to support the carbon. The column was electrically insulated on the interior by a teflon coating and the electrodes were supported on glass laminated strips. Since the Institute had several direct current power supply units, previously used on an electrodialysis project, it had been decided, with agreement from Professor Fabus, to utilize this source of power. Prior to shipment of the unit to the Institute, it was tested by Lowell personnel, using a direct current rectifier, supplied by the Institute.

A diagrammatrical sketch of the unit as it was initially set up and connected at the Appleton Division mill of Consolidated Papers, Inc. is shown in Fig. 51. All materials coming in contact with the condensate were constructed of 316 stainless steel. Four thermocouples were installed midway between each electrode which were initially inserted 6 inches (15.2 cm) or to the center of the column. The connectors to the electrodes, as well as the thermocouples, were insulated from the shell of the column by means of custom-made ceramic insulators. The two condensers used in series consisted of a single tube.

During the adsorption phase the condensate was passed through the condensers and entered the column at the top and exited through the bottom. The column was maintained in a flooded condition by means of a constant level device. During regeneration the vapors were removed from the top of the column through the condensers, except during several trials when the flow was reversed.

As noted in Fig. 51, the three negative electrodes were common to both power sources, with one positive electrode being connected to each power unit. Initially, the column was charged with Filtrasorb 300 activated carbon which had been supplied by Lowell Technological Institute and had been used during their trial period. This was later replaced with Filtrasorb 400 carbon. The unit was never operated successfully and most of the available time was spent operating repeated drying and wetting cycles using tap water. Two runs using condensate were made and the feed for these runs consisted of condensate that had passed through the stripper and also through the furfural column of Mr.

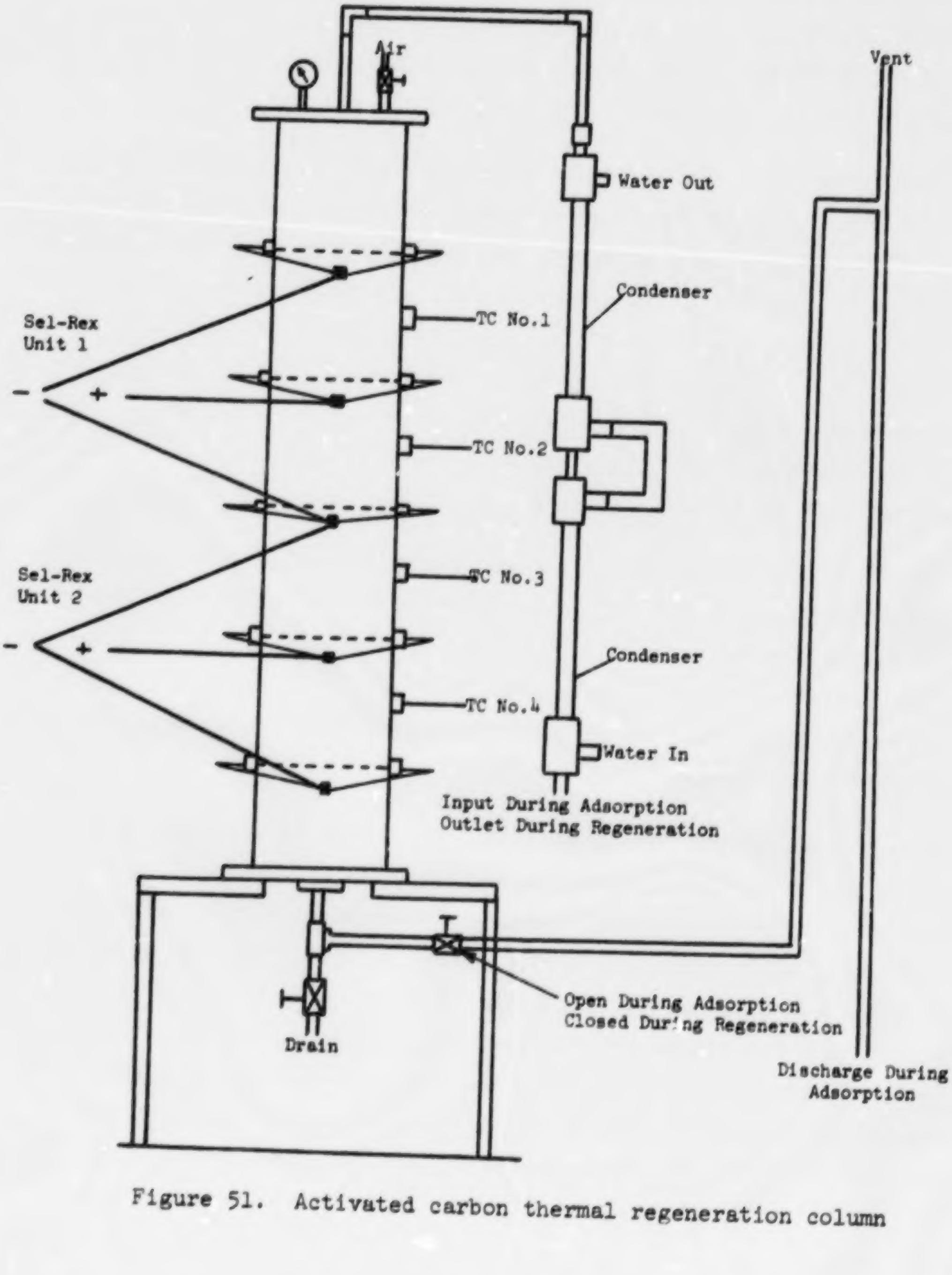

Air
Vent
Water Out
Condenser
Sel-Rex
Unit 1
TC No.1
-
+
TC No.2
Sel-Rex
Unit 2
TC No.3
-
+
Condenser
TC No.4
Water In
Input During Adsorption
Outlet During Regeneration
Open During Adsorption
Closed During Regeneration
Drain
Discharge During
Adsorption

Figure 51. Activated carbon thermal regeneration column

Baierls' system, so that basically most of the SO_2, methanol, and furfural had been removed.

DATA AND DISCUSSION

To simplify the explanation of the data and operation of the column, the procedures will be given in chronological order. Figure 52 is a diagram which labels all of the outlets through the side of the column. All changes made in the electrode hookup and in the location of the thermocouples as the work progressed will be identified by the letters and figures in this sketch. The letters A, B, C, D, and E were the normal outlets for the connectors to the electrodes, while the 1, 2, 3, 4 positions were the original locations of the thermocouples.

The data to be presented will represent only the significant operational changes. Table 19 contains the operating conditions and the temperatures obtained during the operation from January 4 through January 9, 1973. During this time the unit was operated as originally proposed by Lowell Technological Institute and as indicated in Fig. 51; that is, the common cathodes were A, C, and E, while the B anode was connected to Rectifier No. 1 and the D anode to Rectifier No. 2. Prior to activating Rectifier No. 1, the carbon was wet with tap water and drained. Initially, the voltage was set at 75, which produced 55 amps, for a resistance of 0.68 ohms per foot (2.23 ohm/m) of carbon. Within 15 minutes the resistance had increased to 0.89 ohms per foot (2.92 ohm/m) of carbon. After an additional 10 minutes the resistance had increased to 2.02 ohms per foot (6.63 ohm/m), and finally after a total of 35 minutes of operation the resistance was at 28.55 ohms. However, the temperature had risen to 95°C (203°F) after 15 minutes, which is probably at the boiling point of water, since it was later found that the thermocouples were reading low. The second rectifier, which was to heat the bottom 2 foot (61.0 cm) of carbon, was activated 15 minutes after Rectifier No. 1 and approximately boiling temperatures were reached in 10 minutes.

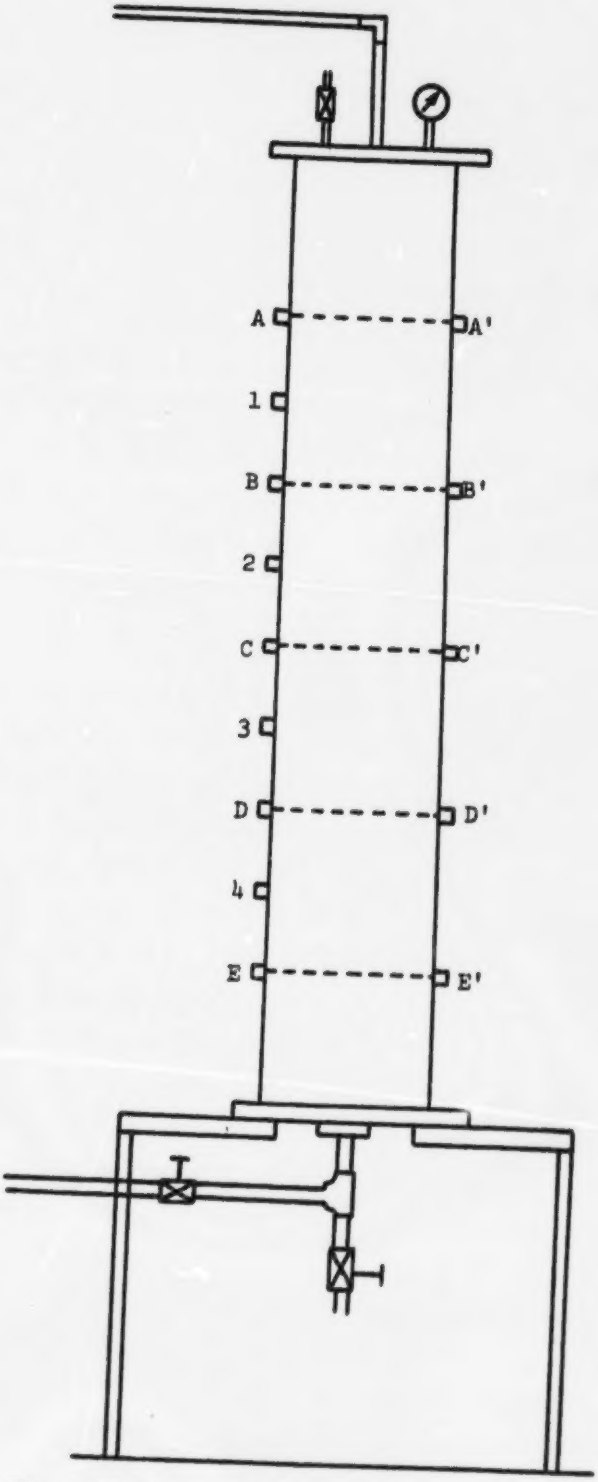

A
A'
1
B
B'
2
C
C'
3
D
D'
4
E
E'

Figure 52. Location of electrode and thermocouple terminals

Table 19. LOWELL UNIT — DIRECT CURRENT

Water Evaporation
Filtrasorb 300 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Rectifier No. 1		Rectifier No. 2		Temperature, °C (°F)			
		Volts	Amps	Volts	Amps	1	2	3	4
		Power connection — cathodes — A, C, & E anodes — B — Rectifier No. 1 — D — Rectifier No. 2							
		Wet column							
1-4-73	10:07	75	55	0	0	20(68)	30(86)	--	--
	10:22	98	55	0	0	95(203)	94(201)	--	--
	10:32	113	28	20	25	--	--	22(72)	29(84)
	10:43	114	2	97	48	95(203)	95(203)	95(203)	95(203)
		Re-wet carbon							
	11:00	115	55	0	0	15(59)	20(68)	16(61)	45(113)
	11:20	115	50	64	77	92(198)	90(194)	28(82)	58(136)
	11:40	115	3	98	5	95(203)	95(203)	95(203)	92(198)
		Re-wet carbon							
	12:00	114	33	0	0	18(64)	26(79)	33(91)	60(140)
	1:10	114	8	0	0	18(64)	25(77)	33(91)	60(140)
		Re-wet carbon							
	2:15	95	5	115	10	94(201)	94(201)	84(183)	84(183)
1-5-73	9:15	50	8	50	27	74(165)	74(165)	74(165)	74(165)
	9:50	50	7	50	15	87(189)	93(199)	93(199)	93(199)
	10:20	75	5	75	2	87(189)	94(201)	94(201)	94(201)
1-8-73	10:40	75	6	75	39	27(81)	27(81)	27(81)	30(86)
	11:10	100	9	100	30	29(84)	91(196)	89(192)	50(122)
	11:30	100	16	100	17	94(201)	94(201)	94(201)	50(122)
	11:50	125	9	116	9	93(199)	93(199)	93(199)	74(165)
	12:25	50	7	50	11	94(201)	94(201)	94(201)	76(169)
	1:25	50	6	50	8	93(199)	93(199)	93(199)	75(167)
	2:05	50	7	50	7	93(199)	91(196)	94(201)	75(167)
	3:10	100	16	0	0	87(189)	85(185)	91(196)	72(162)
	3:30	100	5	0	0	88(190)	83(181)	92(198)	71(160)
		Attempted to dry carbon with stream of air overnight							
1-9-73	9:10	112	6	→ Low amperage (high resistance), removed carbon for inspection of the unit					

The carbon was rewet several times more and following each wetting good amperage was obtained for a short period, after which there would be a sudden increase in resistance. Following the third rewetting, however, at 2:15 p.m. the resistance of No. 1 rectifier was at 4.75 ohms and on No. 2 rectifier at 2.88 ohms and the resistance remained high during the trials of January 5, 1973 and January 8, 1973. On January 9, since the resistance continued to be high, it was decided to remove the carbon for inspection of the unit.

This inspection showed that the electrodes which had been in the positive position were completely covered with a scale or coked carbon material, and that the teflon coating on the interior of the column was blistered extensively. This even extended to the bottom plate. Analysis of the corrosion, which was scraped from the anode electrodes, revealed that on a dried basis, it contained 80.4% ash, 7.8% iron, 9.3% chromium and 1.8% calcium. Thus, it became apparent that the electrodes were literally being disintegrated by electrolysis. It was realized that electrolytic action would result in disintegration when in contact with liquid media, but it was not certain that this would happen in a vapor atmosphere.

The electrodes were cleaned by sand blasting and reinstalled in the column. Initially, one foot (30.5 cm) of carbon was packed into the column and two electrodes connected to Rectifier No. 2; the anode being in the E position and the cathode in the D position. The carbon used was the same that had been removed previously from the column and which had been air dried. Table 20 contains the data obtained. Initially, the resistance was 1.5 ohms per foot (4.92 ohm/m) of carbon but this increased to 13.5 in 15 minutes. During this time a stream of air was fed through the column. Surface temperatures were then determined using a surface pyrometer. The temperatures were very consistent around the periphery of the column. Current was applied for an additional hour, with continued low amperage, after which surface temperatures were again taken. Temperatures were highest in the vicinity of

Table 20. LOWELL UNIT – DIRECT CURRENT

Water Evaporation
Filtrasorb 300 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Rectifier No. 2		Temperature, °C (°F)	Air
		Volts	Amps	4	

Power connection – anode – E
cathode – D
One foot (0.3048 m) of air-dried carbon in column

Date	Time	Volts	Amps	4	Air
1-22-73	8:58	27	18	26(79)	on
	9:08	27	12	35(95)	on
	9:13	27	2	37(99)	on

Location	Surface temperature, °C (°F)			
	Right side	Front	Left side	Back
At D	26.1(79)	25.6(78)	25.0(77)	25.0(77)
Between D & E	27.8(82)	27.8(82)	27.2(81)	26.1(79)
At E	27.8(82)	24.4(76)	27.2(81)	27.8(82)
Below E	26.7(80)	--	--	--

Date	Time	Rectifier No. 2		Temperature, °C (°F)	Air (%)
		Volts	Amps	4	
1-22-73	9:33	50	16	37(99)	50
	9:43	50	13	54(129)	50
	9:53	50	9	57(135)	25
	10:03	50	5	59(138)	0
	10:30	50	7	35(95)	50

Location	Surface temperature, °C (°F)		
	Right side	Front	Left side
Between D & C	42.0(107)	36.7(98)	35.6(96)
At D	42.5(108)	46.8(116)	41.1(106)
Between E & D	36.7(98)	35.6(96)	36.1(97)
At E	30.0(86)	28.3(83)	28.3(83)

Date	Time	Rectifier No. 1		Rectifier No. 2		Temperature, °C (°F)			Air (%)
		Volts	Amps	Volts	Amps	2	3	4	
1-22-73	10:46	0	0	50	8	--	--	34(93)	50
	10:56	0	0	50	6	--	--	27(81)	50

Power connection – cathode – D
anode – C – Rectifier No. 1
– E – Rectifier No. 2
Added second foot of air-dried carbon

Date	Time	Volts	Amps	Volts	Amps	2	3	4	Air (%)
	1:22	50	23	50	18	27(81)	43(109)	21(70)	50
	1:22	50	23	50	32	48(118)	88(190)	38(100)	50

Location	Surface temperature, °C (°F)			
	Right side	Front	Left side	Back
At E	31.1(88)	40.0(104)	26.7(80)	33.9(93)
Between D & E	33.9(93)	42.2(108)	31.1(88)	33.9(93)
At D	44.5(112)	42.2(108)	38.9(102)	47.8(118)
Between C & D	39.0(102)	41.9(107)	35.6(94)	45.0(113)
At C	39.5(103)	36.7(98)	30.6(87)	45.0(113)
Between B & C	33.3(92)	35.6(96)	30.6(87)	33.9(93)
At B	25.6(76)	24.4(76)	25.6(78)	25.6(76)

Removed carbon from column

the D electrode. The current was again turned on for an additional 10 minutes, and then shut off and a second foot (30.5 cm) of air-dried carbon added to the column. Power connections were rearranged so that the cathode from both rectifiers was in the D position, with the anode for Rectifier No. 1 being in the C position and for Rectifier No. 2 in the E position. The current was activated for about 10 minutes at about 50 volts and 23 amps, after which surface temperatures were again taken. The temperatures again were highest around the area of the D electrode as indicated in Table 20. The carbon was then removed from the column.

The column was refilled with Filtrasorb 400 virgin carbon. It was placed in the column in an "as received" condition without previous wetting of the carbon or flooding of the column. Power connections were made so that the A, C, and E positions were anodes and the B position was the cathode for Rectifier No. 1 and the D position was the cathode for Rectifier No. 2. By placing an anode in the A position, it became possible to observe this electrode by removing several inches of carbon. The heating data obtained under these conditions is given in Table 21. Power was on both units for a period of about 35 minutes; voltages of both 50 and 25 were applied with the resistances ranging from 0.18 to 0.25 ohms per foot (0.59-0.82 ohm/m) of carbon in the top 2 feet (61.0 cm) of the column and 0.31 to 0.38 ohms per foot (1.02-1.25 ohm/m) in the bottom 2 feet (61.0 cm). The temperature at No. 1 thermocouple increased from 33 to 193°C (91 to 379°F) during this period, while at No. 4 thermocouple there was no increase. The surface temperatures were again taken and reflected the same heating pattern at the top of the column with very little heating at the bottom. No real hot spots, however, developed. After operating Rectifier No. 2 for 10 minutes, the power connections were changed so that only the bottom foot (30.5 cm) of carbon was being heated. This did result in an increase in temperature at the No. 4 position from 60°C to 210°C (140°F to 410°F). Surface temperatures were fairly even except for a possible hot spot on the left side of the column at the D electrode.

Table 21. LOWELL UNIT — DIRECT CURRENT

Water Evaporation
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Rectifier No. 1		Rectifier No. 2		Temperature, °C (°F)			
		Volts	Amps	Volts	Amps	1	2	3	4

Power connection — anodes — A, C, & E
cathode — B — Rectifier No. 1
— D — Rectifier No. 2

Date	Time	Rectifier No. 1 Volts	Rectifier No. 1 Amps	Rectifier No. 2 Volts	Rectifier No. 2 Amps	1	2	3	4
1-22-73	2:40	50	93	50	65	33(91)	70(158)	84(183)	47(117)
	2:43	50	122	50	72	95(203)	87(189)	88(190)	47(117)
	2:44	25	50	25	33	88(190)	87(189)	86(187)	47(117)
	3:05	25	53	25	37	123(253)	107(225)	96(205)	40(104)
	3:14	25	69	25	40	193(379)	142(288)	116(241)	47(117)

Location	Surface temperature, °C (°F)			
	Right side	Front	Left side	Back
At A	66.8(152)	63.9(147)	63.5(146)	61.8(143)
Between A & B	66.8(152)	58.9(138)	58.5(137)	67.9(154)
At B	66.1(151)	58.5(137)	61.7(143)	67.5(153)
Between B & C	65.0(149)	61.4(142)	63.5(146)	61.7(143)
At C	66.8(152)	54.6(130)	65.0(149)	62.1(144)
Between C & D	61.1(142)	55.0(131)	58.5(137)	53.5(128)
At D	56.1(133)	47.8(118)	53.5(128)	44.5(112)
Between D & E	47.2(117)	41.8(107)	41.8(107)	39.5(103)
At E	34.4(94)	31.1(88)	33.3(92)	31.1(88)

Date	Time	Rectifier No. 1		Rectifier No. 2		Temperature, °C (°F)			
		Volts	Amps	Volts	Amps	1	2	3	4
1-22-73	3:21	0	0	25	37	213(415)	150(302)	126(259)	33(91)
	3:31	0	0	25	38	214(417)	148(298)	157(315)	57(135)

Power connection — D-E only

Date	Time	Rectifier No. 1 Volts	Rectifier No. 1 Amps	Rectifier No. 2 Volts	Rectifier No. 2 Amps	1	2	3	4
	3:35	0	0	25	21	--	--	--	60(140)
	3:50	0	0	50	41	213(415)	147(297)	165(329)	92(198)
	4:20	0	0	75	46	197(387)	154(309)	117(243)	102(216)
	4:33	0	0	75	61	--	--	--	210(410)

Location	Surface temperature, °C (°F)			
	Right side	Front	Left side	Back
At C	90.0(194)	92.3(198)	88.4(191)	91.8(197)
Between C & D	90.0(194)	89.6(193)	91.8(197)	88.4(191)
At D	93.5(200)	89.6(193)	103.3(218)	88.9(192)
Between D & E	88.9(192)	88.4(191)	89.6(193)	88.9(192)
At E	85.0(185)	78.4(173)	75.6(168)	85.6(186)

Heating was continued as shown in Table 22 on the following morning with the power connections the same as previously used. After 10 minutes of operation, during which time there was fairly rapid heating, power was shut off and the column was wet with warm tap water. To facilitate drainage, air was passed through the column for one-half hour. Heating was continued on No. 1 rectifier from 10:15 to 3:55, and during this time the combination of voltages and amperages used represented an electrical resistance of 0.06 to 0.27 ohms per foot (0.20-0.88 ohm/m) of carbon. At the last reading at 3:55, the resistance dropped to 0.18 ohms per foot (0.59 ohm/m). Power was on the No. 2 rectifier from 10:15 to 2:35, at which time the temperature at the No. 3 position suddenly increased from 94°C to 245°C (201°F to 473°F). Electrical resistances during this time were between 0.14 to 0.28 ohms per foot (0.46-0.92 ohm/m) of carbon. Twenty-six liters (6.87 gal.) of water had been vaporized from the column during the 5 3/4 hours of operation.

The following morning on January 24, both power supplies were activated before wetting the carbon. No. 1 rectifier was then producing 32 volts at 50 amps, while No. 2 rectifier produced 47 volts at 50 amps. The column was flooded and drained with the aid of air pressure, during which time 17 liters (4.49 gal.) of water were drained from the column which is the amount of non-adsorbed water in the column when it is in a flooded state. Current was placed on No. 1 rectifier for 20 minutes prior to turning on the No. 2 rectifier. Initially, the resistance was very low, there being 13 volts on Rectifier No. 1 producing 75 amps, while on No. 2 rectifier there were 100 amps and 37 volts. However, shortly after the No. 2 rectifier was energized, a sudden drop in amperage was noted and all power was disconnected. The No. 2 rectifier was then connected to the two bottom electrodes between the bottom foot (30.5 cm) of carbon, the anode being in the D position and the cathode in the E position. This configuration provided 53 amps at 52 volts. Connections were then changed to the anode in the C position and the cathode in the E position on Rectifier No. 2 which included 2

Table 22. LOWELL UNIT — DIRECT CURRENT

Water Evaporation
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Rectifier No. 1		Rectifier No. 2		Temperature, °C (°F)			
		Volts	Amps	Volts	Amps	1	2	3	4
Power connection — anodes — A, C, & E cathodes — B — Rectifier No. 1 — D — Rectifier No. 2									
1-23-73	8:43	25	50	25	25	33(91)	33(91)	36(97)	35(95)
	8:48	25	60	25	27	70(158)	57(135)	50(122)	54(129)
	8:53	0	0	25	27	75(167)	60(140)	58(136)	66(151)
Wet carbon with warm tap water									
	10:15	6	50	0	0	17(63)	31(88)	41(106)	44(111)
	11:05	11	83	0	0	56(133)	66(151)	41(106)	44(111)
	11:15	11	82	16	50	66(151)	76(169)	47(117)	50(122)
	11:35	11	77	22	76	83(181)	89(192)	70(158)	70(158)
	12:35	11	66	22	56	79(174)	92(198)	91(196)	91(196)
	1:15	18	101	27	57	92(198)	92(198)	91(196)	90(194)
	1:35	18	107	42	77	91(196)	91(196)	91(196)	90(194)
	2:05	18	102	53	93	92(198)	92(198)	94(201)	93(199)
	2:35	18	76	58	130	90(194)	86(187)	245(473)	140(284)
	2:45	18	66	0	0	90(194)	88(190)	250+(482)	212(414)
	3:05	24	68	0	0	92(198)	92(198)	250+(482)	235(455)
	3:25	50	91	0	0	123(253)	103(217)	250+(482)	243(469)
	3:55	50	137	0	0	112(234)	164(327)	250+(482)	233(451)
26 (6.87 gal) Liters vaporized from column									
1-24-73	8:58	32	50	47	50	37(99)	47(112)	44(111)	52(126)
Wet carbon with tap water									
	9:50	13	75	0	0	21(70)	43(109)	48(118)	51(124)
	10:10	17	100	0	0	45(113)	68(154)	50(122)	51(124)
	10:36	17	92	37	100	71(160)	92(198)	92(198)	60(140)
Sudden drop in amperage on No. 2 rectifier Power connection — anode — D cathode — E — Rectifier No. 2									
	11:07	0	0	52	53	—	—	—	—
Power connection — anode — C cathode — E — Rectifier No. 2									
	—	0	0	—	95	Immediate drop in amperage			
Power connection — anode — D cathode — E — Rectifier No. 2									
	11:14	0	0	53	10	—	—	—	—
	11:21	0	0	53	6	89(192)	90(194)	91(196)	91(196)
Power connection — anode — B cathode — D — Rectifier No. 2									
	—	0	0	52	12	—	—	—	—
Power connection — anode — B cathode — D — Rectifier No. 1									
	11:44	62	35	0	0	—	—	—	—
Wet carbon with tap water Power connection — same as on 1-23-73 above									
	2:55	17	75	0	0	47(112)	47(112)	80(176)	86(187)
	3:45	17	75	0	0	91(196)	91(196)	75(167)	80(176)
	3:55	17	75	32	50	91(196)	91(196)	76(169)	80(176)
	4:15	17	75	32	32	91(196)	91(196)	91(196)	91(196)
	4:25	18	75	0	0	91(196)	91(196)	90(194)	89(192)
¼-Lb pressure applied to column — momentary increase in amperage on Rectifier No. 2									
	4:40	18	75	0					
10 Lb/in² (0.7 kg/cm²) pressure applied to column — momentary increase in amperage on Rectifier No. 2									

feet (61.0 cm) of carbon. Amperage started at 95 and immediately dropped to a very low level. Again the connections were changed so that only the bottom foot (30.5 cm) of carbon was involved, with the anode in the D position and the cathode in the E position. With this configuration at 11:14 a.m. the readings were 53 volts and 10 amps and by 11:21 the amperage had dropped to 6. The rectifier was then connected between the middle 2 feet (61.0 cm) of carbon, with the anode in the B position and the cathode in the D position. The power readings were then 52 volts and 12 amps. With the same electrode connections, but to the No. 1 rectifier instead of No. 2 rectifier, the readings were 62 volts and 35 amps.

These changes indicated that there may have been a separation of the carbon at some point in the column, so again the carbon was wet with tap water. All power connections were then replaced as previously, with the anodes in the A, C, and E position and the cathode for Rectifier No. 1 in the B position and for Rectifier No. 2 in the D position. While in the wet condition, resistance remained low. Prior to discontinuing operation for the day, pressure was exerted on the column, first at 3/4 pounds per square inch (0.052 kg/cm^2) and then at 10 pounds per square inch (0.70 kg/cm^2), by closing off all outlet vents. Each time there was a momentary increase in amperage on Rectifier No. 2.

Operational data for the next day's operation, January 25, are given in Table 23. Power connections were left the same as the previous day. The carbon was again wet with tap water and power was applied for one hour. During that time there was a rapid heating to near the boiling point with good conductivity while the carbon was wet. The vapor flow was then reversed to top to bottom on the assumption that this might produce some internal pressures that would tend to pack the carbon rather than loosen it. The amperages on No. 1 rectifier dropped considerably and the application of 3 pounds per square inch (0.21 kg/cm^2) of air pressure did not restore the amperage.

Table 23. LOWELL UNIT — DIRECT CURRENT

Water Evaporation
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

<table>
<tr><th rowspan="2">Date</th><th rowspan="2">Time</th><th colspan="2">Rectifier No. 1</th><th colspan="2">Rectifier No. 2</th><th colspan="4">Temperature, °C (°F)</th></tr>
<tr><th>Volts</th><th>Amps</th><th>Volts</th><th>Amps</th><th>1</th><th>2</th><th>3</th><th>4</th></tr>
<tr><td colspan="10">Power connection — anodes — A, C, & E
cathodes — B — Rectifier No. 1
— D — Rectifier No. 2
Wet carbon with tap water</td></tr>
<tr><td>1-25-73</td><td>9:02</td><td>22</td><td>74</td><td>32</td><td>50</td><td>22(72)</td><td>43(109)</td><td>50(122)</td><td>53(122)</td></tr>
<tr><td></td><td>9:20</td><td>19</td><td>75</td><td>13</td><td>25</td><td>38(100)</td><td>50(133)</td><td>69(156)</td><td>68(154)</td></tr>
<tr><td></td><td>9:50</td><td>19</td><td>70</td><td>12</td><td>25</td><td>85(185)</td><td>91(196)</td><td>86(187)</td><td>81(178)</td></tr>
<tr><td></td><td>10:00</td><td>33</td><td>15</td><td>28</td><td>42</td><td>91(196)</td><td>91(196)</td><td>91(196)</td><td>88(190)</td></tr>
<tr><td colspan="10">Reversed vapor flow from top to bottom</td></tr>
<tr><td></td><td>10:10</td><td>34</td><td>12</td><td>28</td><td>18</td><td>91(196)</td><td>91(196)</td><td>91(196)</td><td>91(196)</td></tr>
<tr><td colspan="10">10-Lb/in² (0.7 kg/cm²) air pressure on column — momentary increase in amperage
Wet carbon with tap water</td></tr>
<tr><td></td><td>10:47</td><td>32</td><td>75</td><td>0</td><td>0</td><td>62(144)</td><td>70(158)</td><td>67(153)</td><td>64(147)</td></tr>
<tr><td></td><td>11:10</td><td>34</td><td>12</td><td>44</td><td>75</td><td>76(169)</td><td>90(194)</td><td>91(196)</td><td>91(196)</td></tr>
<tr><td colspan="10">3-Lb/in² (0.21 kg/cm²) air pressure on column — no increase in amperage
Removed carbon and cleaned electrodes</td></tr>
<tr><td colspan="10">Refilled column with 4 ft (1.219 m) of Filtrasorb 400 carbon
Wet carbon</td></tr>
<tr><td>1-30-73</td><td>8:17</td><td>31</td><td>50</td><td>27</td><td>50</td><td>36(97)</td><td>38(100)</td><td>37(99)</td><td>36(97)</td></tr>
<tr><td></td><td>8:35</td><td>75</td><td>6</td><td>68</td><td>6</td><td>57(135)</td><td>57(135)</td><td>59(138)</td><td>78(172)</td></tr>
<tr><td colspan="10">Shell of column hottest at No. C electrode
Isolated C electrode — no improvement in top foot
Ran steam through carbon to dispel air</td></tr>
<tr><td></td><td>9:20</td><td>45</td><td>34</td><td>36</td><td>35</td><td>93(199)</td><td>93(199)</td><td>93(199)</td><td>94(201)</td></tr>
<tr><td></td><td>9:30</td><td>45</td><td>27</td><td>36</td><td>32</td><td>93(199)</td><td>92(198)</td><td>92(198)</td><td>92(198)</td></tr>
<tr><td colspan="10">Drop off in amperage
Tamped top foot (0.305 m) of carbon</td></tr>
<tr><td></td><td>--</td><td>27</td><td>76</td><td>36</td><td>20</td><td>--</td><td>--</td><td>--</td><td>--</td></tr>
<tr><td colspan="10">Removed carbon from column</td></tr>
</table>

The carbon and electrodes were again removed from the column and again the positive or anode electrodes were found to be corroded. The electrodes were again cleaned by sand blasting, replaced in the column and the column refilled with Filtrasorb 400 carbon. The column was flooded with tap water and allowed to drain overnight.

The electrodes were connected as previously and current turned on at 8:17 a.m. on January 30. The wet carbon showed low resistance, there being 31 volts and 50 amps on the No. 1 rectifier and 27 volts and 50 amps on the No. 2 rectifier, but within 20 minutes the amperage had dropped to 6 on both rectifiers. It was found that the surface temperature was hottest at the C electrode. This electrode was then disconnected from the system but there was no real improvement. Steam was then passed through the carbon to dispel any air, but again there was a relatively rapid drop off in amperage. Amperage on the No. 1 rectifier, however, did increase upon tamping the top one foot (30.5 cm) of carbon. The power was then shut off and the carbon removed from the column. It was decided that it was useless to continue with direct current using stainless steel anodes. It would be necessary to use platinized electrodes as anodes in order to successfully use direct current.

In preparation for using alternating current on the unit, the electrodes were again cleaned. The work using direct current had indicated that proper carbon packing was very important. This was almost impossible to do with the electrode supports as originally designed, since all five electrodes had to be inserted into the column together and tamping through the electrode slots was next to impossible. Consequently, the glass laminate electrode supports were cut in two places so that no more than two electrodes had to be inserted at one time. Using air-dried carbon, the bottom foot (30.5 cm) of the column was filled and packed with a small wood ram rod. Following the packing of the carbon, the leads from one of the direct current rectifiers were connected to the D and E electrodes. This was done in order to obtain the voltage and amperage readings for calculation of the resistance. After packing the bottom foot (30.5 cm), the voltage was 8 and the amperage 25, for a resistance of 0.32 ohm per foot (1.05 ohm/m) of carbon. Packing on the second foot (30.5 cm) of carbon in a like manner and connecting the electrodes in the C and D position produced the same resistance. After packing the third foot (30.5 cm) of carbon, the resistance was 0.68 ohm, and since this was double the resistance in the first two feet (61.0 cm), packing was continued until the resistance was at 0.28 ohm. The top foot (0.3048 m) of carbon after packing had a resistance of 0.28 ohm (0.92 ohm/m).

It had also been necessary to make other repairs and changes to the column. Shortly after operation of the column was initiated, inspection had shown that a considerable portion of the teflon coating had blistered. These blisters were not immediately broken and the column was used in that condition; however, when they did break, repairs were made with high-temperature electrical insulation tape. The ceramic electrode and thermocouple insert insulators also gradually cracked and failed and they were replaced with a machined insulator constructed from nylon. While nylon has a rather low melting point, these insulators were easily fabricated and acted as a safety valve if localized hot spots developed.

A 440-volt transformer with a step output between 110 and 220 volts was obtained for an alternating current power source. A carbon disk rheostat was also placed in the line in order to obtain voltages below 110 when desired. Having only a single power source, however, did provide disadvantages in that operation flexibility was considerably handicapped. It was thus necessary to pass the current through 4 feet (1.219 m) of carbon with a single unit rather than through 2 feet (61.0 cm) each with two units, as done when using direct current.

The data for the first operation using alternating current are given in Table 24.

Power connections were made between A and E and the other three electrodes were allowed to "float" in the system. Power was on the column

Table 24. LOWELL UNIT – ALTERNATING CURRENT

Water Evaporation
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Volts	Amps	Temperature, °C (°F)				Elec. resistance	
				1	2	3	4	ohms/ft	ohm/meter

Power connection -- A to E
Wet carbon

Date	Time	Volts	Amps	1	2	3	4	ohms/ft	ohm/meter
2-5-73	1:27	109	56	33(91)	30(86)	32(90)	32(90)	0.42	1.38
	1:47	109	64	79(174)	67([illegible])	80(176)	82(180)	0.42	1.38
	1:57	109	52	85(185)	84(183)	83(181)	86(187)	0.52	1.71

Location	Surface temperature, °C (°F)			
	Right side	Front	Left side	Back
At A	57.2(135)	46.7(116)	55.6(132)	55.6(132)
Between A & B	51.1(124)	50.0(122)	53.3(128)	62.2(144)
At B	47.8(118)	47.8(118)	52.8(127)	57.8(136)
Between B & C	53.3(128)	50.0(122)	54.4(130)	58.9(138)
At C	86.7(188)	83.9(183)	88.9(192)	85.0(185)
Between C & D	86.1(187)	83.3(182)	84.4(202)	83.9(183)
At D	69.4(157)	63.3(146)	78.3(173)	75.0(167)
Between D & E	74.4(166)	67.2(153)	83.9(183)	80.6(177)
At E	53.3(128)	58.9(138)	56.1(133)	58.9(138)

Date	Time	Volts	Amps	Temperature, °C (°F)				Elec. resistance	
				1	2	3	4	ohms/ft	ohm/meter
2-5-73	2:17	109	47	82(180)	78(172)	81(178)	82(180)	0.58	1.90
	2:53	124	48	88(190)	88(190)	87(189)	84(183)	0.64	2.10
	3:21	152	73	107(225)	88(190)	96(205)	88(190)	0.52	1.71

Location	Surface temperature, °C (°F)			
	Right side	Front	Left side	Back
At A	81.1(178)	81.1(178)	83.3(182)	83.9(183)
Between A & B	79.4(175)	83.9(183)	87.8(190)	88.9(192)
At B	88.9(192)	86.7(188)	85.6(186)	88.9(192)
Between B & C	90.0(194)	90.0(194)	89.4(193)	88.9(192)
At C	91.1(196)	91.1(196)	90.6(195)	86.1(187)
Between C & D	90.0(194)	89.4(193)	91.1(196)	89.9(194)
At D	91.1(196)	91.1(196)	91.1(196)	81.1(178)
Between D & E	92.2(198)	90.6(195)	89.4(193)	89.4(193)
At E	66.7(152)	77.8(172)	64.4(148)	66.7(152)

Date	Time	Volts	Amps	Temperature, °C (°F)				Elec. resistance	
				1	2	3	4	ohms/ft	ohm/meter
Power connection – A to C & E to C									
2-5-73	4:00	109	180	99(210)	87(189)	95(203)	92(198)	0.15	0.49
Readings E to C only									
	--	109	40	127(261)	96(205)	99(210)	99(210)	1.36	4.46
Power connection B to E									
	4:23	173	61	107(225)	97(207)	100(212)	100(212)	0.94	3.08
	4:33	173	61	104(219)	101(214)	169(336)	108(226)	0.94	3.08
Wet Column – Power connection A to E									
2-6-73	10:51	113	40	16(61)	16(61)	17(63)	18(64)	0.71	2.33
	11:40	156	42	85(185)	88(190)	84(183)	77(171)	0.93	3.05
	11:50	156	11	84(183)	84(183)	83(181)	82(180)	3.54	11.61
	12:20	158	21	88(190)	87(189)	87(189)	78(172)	1.88	6.17
	12:40	157	--	88(190)	87(189)	260+(500+)	77(171)	--	
Power off for ten minutes									
	12:58	156	129	86(187)	88(190)	163(325)	75(167)	0.30	0.98
	1:10	156	24	85(185)	85(185)	190(374)	77(171)	1.62	5.32
	1:20	156	32	86(187)	85(185)	191(376)	78(172)	1.22	4.00

Removed carbon from column

for one-half hour at a voltage of 109 and amperage between 52 and 66, which indicated an electrical resistance of 0.42 to 0.52 ohm per foot (1.38-1.71 ohm/m) of carbon. Surface temperatures taken at the end of one-half hour operation are given in Table 24, and they indicate that the column did not heat in a uniform manner. Temperatures around the C location were considerably higher than either the top or bottom, although the internal thermocouples did not register this variation.

The unit was operated for an additional hour during which time the temperatures rose only very slowly, except in the No. 1 position. which registered 107°C (225°F). During this time, electrical resistance was between 0.52 and 0.64 ohm per foot (1.71-2.10 ohm/m) of carbon. Surface temperatures were then read and, although there were not any hot spots, the center of the column was considerably higher than either end, with the bottom being the coolest.

An attempt was made to split the current by making connections between A and C and E and C. With this configuration, the temperature at the No. 1 thermocouple rose very rapidly to 127°C (261°F). Because of this, the power connections were changed to B to E to attempt to heat only the bottom 3 feet (91.4 cm) of carbon. With the transformer output set at 173 volts, there was a current flow of 61 amps, which was equivalent to 0.94 ohm resistance per foot (3.08 ohm/m). During the 10 minutes of operation, the temperature rose at the No. 3 thermocouple location from 100°C to 169°C (212°F to 336°F).

On the morning of February 6, the column was again flooded with tap water and drained. A stream of air was admitted to the bottom of the column, but no attempt was made at the exact measurement of the air. Air was used periodically through various trials, but at no time did it appear to have much effect, either favorably or adversely. The transformer was again connected over the entire 4 feet (1.2192 m) of carbon at A and E electrodes. During the first hour of operation, electrical resistance changed from 0.71 to 3.54 ohms with a gradual increase in the temperatures to around the 80°C (176°F) level. At the end of 50 more minutes of operation, the temperature at the No. 3 thermocouple suddenly increased to 260+°C (500+°F) and the power turned off for ten minutes. At 12:55 p.m. the electrical resistance was 0.30 ohm per foot (0.98 ohm/m) but increased to 1.62 ohms within 15 minutes. After 1:20 p.m. the unit was shut down and the carbon removed so that the three unused electrodes could be taken out of the system.

The A and E electrodes were cleaned with steelwool prior to reinstalling in the column. The cleaning may not have been necessary as there was no evidence of the previous extensive corrosion which resulted when using the direct current. The column was then filled with water and the carbon slowly added and allowed to settle without any physical packing, excess water being drained from the bottom. The data for this operation will be found in Table 25. The unit was operated for 1 hour and 10 minutes with the top flange removed, and during this time the temperature at the No. 1 thermocouple increased from 32 to 100°C (90 to 212°F), at the No. 2 thermocouple from 32 to 84°C (90 to 183°F), at the No. 3 thermocouple from 34 to 50°C (93 to 122°F) and at the No. 4 thermocouple from 29 to 94°C (94 to 201°F). The resistance was around 1.25 ohms per foot (4.10 ohms/m) of carbon. From 1:10 p.m. until 3:05 p.m. operation was with the top flange in place, and the electrical resistance varied between 1.70 and 4.30 ohms per foot (5.58-14.11 ohms/m) of carbon. It was suspected that the increase in electrical resistance was caused by loose packing of the carbon, so the side of the column was tapped with a mallet and immediately the amperage decreased to zero. Upon removal of the top flange it was found that the carbon had settled below the top electrode. Carbon was added and operation was started without the top flange and with an electrical resistance of 0.62 ohm per foot (2.03 ohms/m) of carbon. All temperatures were at 100°C (212°F) and the vapors were being removed from the top of the column directly to the atmosphere.

The following day on February 8, column operation was continued and the entire day was spent in repeatedly tapping the column and adding carbon as necessary as the carbon packed following continued drying.

Table 25. LOWELL UNIT — ALTERNATING CURRENT

Water Evaporation
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (0.3048 × 1.291 m)

Date	Time	Volts	Amps	Temperature, °C (°F)				Elec. resistance	
				1	2	3	4	ohms/ft	ohm/meter
Power connection A to E (clean electrodes), other electrodes removed Wet carbon — top flange off									
2-7-73	11:45	110	25	32(90)	32(90)	34(93)	29(84)	1.10	3.61
	12:45	110	22	97(207)	76(169)	48(118)	94(201)	1.25	4.10
	12:55	110	22	100(212)	84(183)	50(122)	94(201)	1.25	4.10
Top flange in place									
	1:50	138	20	101(214)	98(208)	58(136)	101(214)	1.80	5.90
	2:12	138	24	99(210)	100(212)	99(210)	100(212)	1.44	4.72
	2:25	138	8	99(210)	99(210)	98(208)	97(207)	4.30	14.11
	3:05	138	14	100(212)	100(212)	100(212)	100(212)	2.46	8.07
Tapped side of column — amperage decreased to 0 — carbon settled below top electrode — added carbon — left top flange off									
	3:40	124	50	100(212)	100(212)	100(212)	100(212)	0.62	2.03
Power off									
2-8-73	8:24	123	29	46(115)	48(118)	49(120)	47(117)	1.06	3.48
	8:30	124	17	56(133)	54(129)	54(129)	52(126)	1.82	5.97
Tapped column with mallet repeatedly									
	8:40	125	27	64(147)	60(140)	60(140)	56(133)	1.15	3.77
	8:50	124	44	85(181)	72(162)	68(154)	62(144)	0.71	2.33
	9:20	126	32	111(232)	101(214)	99(210)	100(212)	0.98	3.22
Added carbon repeatedly as needed									
	10:00	126	32	115(239)	102(216)	98(208)	100(212)	0.98	3.22
	10:30	124	32	113(235)	102(216)	93(199)	100(212)	0.97	3.18
	11:10	126	29	127(261)	108(226)	100(212)	100(212)	1.09	3.58
	11:50	126	28	162(324)	113(235)	109(228)	102(216)	1.12	3.67
Power off during noon hour									
	1:40	124	36	200(392)	116(241)	112(234)	103(217)	0.86	2.82
Intermittent power									
	3:27	124	37	251(484)	188(370)	118(244)	107(225)	0.84	2.76
Power on continuously									
	3:49	124	42	132[a](270)	232(450)	163(325)	109(228)	0.74	2.43
	4:30	124	78	102[b](216)	203[a](397)	120[b](248)	260(500)	0.40	1.31
	4:45	123	127	102[b](216)	107[b](225)	165[b](329)	203[a](397)	0.24	0.79
Set thermocouples 2½ inches (6.4 cm) into column Wet carbon — when adding water side cork blew out (unused electrode site) Lost dry carbon through opening — added carbon — top flange on									
2-9-73	9:43	115	73	28(82)	28(82)	28(82)	34(93)	0.39	1.28
	9:55	111	22	40(104)	35(95)	35(95)	42(108)	1.26	4.13
	10:43	111	55	100(212)	100(212)	81(178)	100(212)	0.50	1.64
	11:05	128	58	102(216)	101(214)	101(214)	101(214)	0.55	1.80
Hydrogen sulfide odor									
	11:45	140	37	100(212)	100(212)	100(212)	100(212	0.94	3.08
Small hole blown through side of column — shut down									

---

[a] Thermocouple inserted 3 inches (7.6 cm) into column.

[b] Thermocouple inserted 1½ inches (3.8 cm) into column.

By 1:40 p.m., however, the temperature at the No. 1 position was at 200°C (392°F) and the power was on intermittently for a period of 1 hour and 15 minutes in an attempt to raise the temperature of the lower portions of the column without increasing the temperature unduly at the No. 1 station. The No. 1 thermocouple was then partly removed from the column so that it was inserted into the column for only 3 inches (7.62 cm) instead of the previous 6 inches (15.24 cm). It immediately registered a temperature of only 132°C (270°F), indicating that the temperature of the carbon was high only at the center. As the temperatures increased in the interior at the other stations, these thermocouples were also brought closer to the periphery of the column, and in this way the carbon was practically completely dried out without raising the temperature at the periphery, where excessive high temperatures would probably damage the teflon insulation.

Following this operation the column was probably packed as good as possible but it was decided to proceed through one more drying cycle before applying acetic acid to the carbon. All four thermocouples were set so that they extended 2 1/2 inches (6.35 cm) into the carbon. Wetting of the carbon was started by passing water into the top of the column; however, the increased pressure upon the sides of the column caused one of the small corks, which had been used to close up the opening when the three center electrodes had been removed, to blow out. This cork was in the B position and the dry carbon being very fluid rapidly poured through this opening, with the result that about half of the top foot (30.5 cm) of carbon flowed from the column. The opening was again closed and all stoppers tightly secured and the carbon replaced and packed as well as possible. Flooding of the column was continued until all of the carbon was considered to be wetted. As will be seen later, this was not the case.

With the top flange in place, heating was started at 9:33 a.m. on February 9, with an electrical resistance of 0.39 ohm per foot (1.28 ohm/m) of carbon. By 10:45 a.m. the No. 1, 2, and 4 thermocouples registered 100°C (212°F) while the No. 3 thermocouple registered 81°C

(178°F), by 11:05 a.m. all temperatures were at the boiling point of water and the resistance remained fairly low at 0.55 ohm. At this point in time, however, what appeared to be a hydrogen sulfide odor was noticeable, but its source could not be traced. At about 11:45 a.m. the resistance had increased to 0.94 and a small jet of steam was suddenly released from the side of the column.

The carbon was removed for inspection of the column and it became evident that localized heating had volatilized a small portion of the teflon coating, which then resulted in a short circuit or arcing directly to the shell of the column, with a subsequent breakthrough. Evidently because of the previous disruption of the packed column, which had resulted in uneven packing, the water had channeled through the column, and one side was not wetted. Thus, this portion of the dry carbon immediately became very hot, with the beforementioned results.

The column was repaired, charged with 4 feet (1.2192 m) of new Filtrasorb 400 carbon by adding the carbon to a flooded column and then draining. Power connections were made between the B and E position so that the top foot (30.5 cm) of carbon would not be heated directly by the electric current. The thermocouples were placed so that No. 1 was in the No. 1 position 2 inches (5.08 cm) into the column, No. 2 in the C' position 6 inches (15.24 cm) into the column, No. 3 in the No. 3 position 2 inches (5.08 cm) into the column, and No. 4 in the D' position 2 inches (5.08 cm) into the column. A vibrator was also installed on the outside of the shell of the column to facilitate packing. The data obtained when operating under these conditions are shown in Table 26. Operation during February 16 and 19 then resulted in gradual drying and packing of the carbon. By 3:10 p.m. on the 19th the carbon was completely dry, except for about one inch (2.54 cm) around the periphery of the column.

On February 20 the column was again wet, with power connections to the B and E positions and the thermocouples placed the same as for February 16. By 2:15 p.m. 23.5 liters (6.21 gal.) of water had been distilled

Table 26. [illegible]WELL UNIT — ALTERNATING CURRENT

Water Evaporation
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Volts	Amps	Temperature, °C (°F) 1	2	3	4	Elec. resistance ohms/ft	ohm/meter
Power connection B to E — vibrator installed on shell of column Thermocouple configuration: 1 — No. 1 position, 2 inches (5.1 cm) into column 2 — C' position, 6 inches (15.2 cm) into column 3 — No. 3 position, 2 inches (5.1 cm) into column 4 — D' position, 2 inches (5.1 cm) into column									
Virgin carbon — wet									
2-16-73	1:35	110	32	41(106)	42(108)	40(104)	41(106)	1.15	3.77
	2:05	110	10	41(106)	82(180)	72(162)	75(163)	3.67	12.04
Started vibrator and tapped column with mallet									
	2:15	111	21	41(106)	86(187)	72(162)	74(165)	1.76	5.77
	2:55	110	6	74(165)	81(178)	71(160)	71(160)	6.05	19.85
Packed carbon from top									
	3:25	109	71	74(165)	85(185)	79(172)	78(172)	0.51	1.67
	4:30	110	45	100(212)	99(210)	99(210)	99(210)	0.81	2.66
Power off									
2-19-73	8:15	108	27	36(97)	36(97)	36(97)	36(97)	1.33	4.36
Packed carbon from top									
	9:05	106	83	38(100)	58(136)	55(131)	53(127)	0.43	1.31
	9:25	106	54	100(212)	108(226)	100(212)	100(212)	0.65	2.13
	10:05	108	33	99(210)	110(230)	100(212)	98(210)	1.09	3.78
Packed carbon from top									
	10:35	106	50	100(212)	110(230)	101(214)	95(203)	0.71	2.33
Sudden temperature rise on No. 2 thermocouple to 143°C (289°F) then to 181°C (358°F) Removed top flange — packed carbon — No. 1 thermocouple out of order — flange left off									
	1:35	58	35	—	164[a](327)	118(244)	100(212)	0.55	1.80
	2:40	65	47	—	166[b](331)	160(320)	105(221)	0.46	1.51
	3:10	65	59	—	98[c](208)	106[c](223)	96[c](205)	0.37	1.21
Power off — carbon dry except for 1 (2.5 cm) inch around periphery									
Wet carbon — replaced top flange Power connection B to E — thermocouple configuration same as for 2-16-73									
2-20-73	9:00	88	125	24(75)	31(88)	28(82)	35(95)	0.27	0.88
	9:50	95	100	97(207)	79(174)	96(205)	95(203)	0.32	1.05
	10:30	105	57	98(208)	95(203)	98(208)	103(217)	0.61	2.00
Vibrator on									
	10:40	107	44	98(208)	97(207)	99(210)	105(221)	0.81	2.66
	11:30	107	33	98(208)	100(212)	101(214)	157(315)	1.08	3.54
Vibrator off									
	12:00	108	31	98(208)	102(216)	102(216)	151(304)	1.16	3.80
	1:00	107	36	99(210)	133(272)	105(221)	134[d](273)	0.99	3.25
	2:00	106	56	99(210)	147[b](297)	120(248)	162[e](324)	0.63	2.07
	2:15	80	53	98(208)	101[c](214)	192(378)	192[e](378)	0.50	1.64
Power off — 23½ liters (6.2 gal) of water distilled from column and 5 liters (1.32 gal.) drained									

---

[a] Thermocouple inserted 4 inches (10.2 cm) into column.

[b] Thermocouple inserted 3 inches (7.6 cm) into column.

[c] Thermocouple inserted 1½ inches (3.8 cm) into column.

[d] Thermocouple inserted 1 inch (2.5 cm) into column.

[e] Thermocouple inserted ½ inch (1.3 cm) into column.

from the carbon and 5 liters (1.32 gal.) had been collected at the bottom of the column. It was then decided that the column was ready for adsorption of acetic acid.

The first run in which acetic acid was adsorbed on the carbon was made on February 21. Condensate that had been steam stripped and passed through the furfural carbon adsorption column was used as feed. Thus, this condensate had most of the SO_2, methanol, and furfural removed. The column was fed at 1.66 liters (0.44 gal.) per minute, which is equivalent to 22.75 liters per minute per square meter (0.559 gallon per minute per square foot). 1576 Grams (3.48 pounds) of acetic acid were adsorbed on the carbon. The following day, February 22, an attempt at regenerating the column was made. The regenerating data are found in Table 27. Power connections were in the B and E position, which resulted in one foot (0.3048 m) of carbon not being heated by the electric current. The thermocouples were placed in the following position: No. 1 in the No. 1 position 2 inches (5.08 cm) into the carbon, No. 2 in the C' position 6 inches (15.24 cm) into the carbon, No. 3 in the No. 3 position 2 inches (5.08 cm) into the carbon, and No. 4 in the D' position 2 inches (5.08 cm) into the carbon. Heating was continued for 7 hours during which time 21.62 liters (5.71 gal.) of water were evaporated, which contained 89.14 grams (0.20 lb) of acetic acid. The temperature at the No. 2 thermocouple, which was in the center of the carbon, rose to 218°C (424°F) after 2 hours and 20 minutes of operation. This thermocouple was then gradually moved toward the periphery of the column, in order to more closely watch the temperature pattern. Since the top foot (30.5 cm) of carbon was not heated directly, its temperature never rose above the boiling point. The higher temperatures at the No. 2 and 4 thermocouples indicated that the left side of the column was heating much faster than the right side.

The second absorption run was made prior to obtaining all of the analytical data from the regeneration of Run 1, and it was not known at that time that such a very small amount of acetic acid had been removed from the column. However, with a feed rate of 1.74 liters (0.46 gal.)

Table 27. LOWELL UNIT — ALTERNATING CURRENT

Run 1 — Desorption or Regeneration
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Volts	Amps	Temperature, °C (°F)				Elec. resistance		Sample No.	Sample size, liters	Volatile organic acids	
				1	2	3	4	ohms/ft	ohm/meter			Concentration, g/l	Removed, g
2-21-73	Acetic acid adsorbed on carbon — 1576 grams or 3.48 lbs												
2-22-73	Power connection B to E Thermocouple configuration: 1 — No. 1 position, 2 inches (5.1 cm) into carbon 2 — C' position, 6 inches (15.2 cm) into carbon 3 — No. 3 position, 2 inches (5.1 cm) into carbon 4 — D' position, 2 inches (5.1 cm) into carbon												
	8:20	100	100	40(104)	36(97)	40(104)	40(104)	0.33	1.08	—	—	—	—
	8:50	102	107	100(212)	96(205)	99(210)	98(208)	0.30	1.98	—	—	—	—
	9:00	103	87	100(212)	99(210)	100(212)	100(212)	0.39	1.28	1	2.00	4.22	8.44
	9:20	109	71	100(212)	109(228)	98(208)	99(210)	0.51	1.67	2	2.00	4.25	8.50
	9:30	110	44	98(208)	140(284)	100(212)	99(210)	0.83	2.72	3	2.00	4.86	9.72
	9:50	106	28	100(212)	167(333)	98(208)	99(210)	1.23	4.04	4	2.00	4.26	8.52
	10:40	122	21	100(212)	218(424)	99(210)	100(212)	1.94	6.36	5	2.00	4.12	8.24
	11:20	135	21	101(214)	204[a](399)	100(212)	103(217)	2.14	7.02	6	2.00	4.02	8.04
	12:10	137	22	100(212)	160[b](320)	98(208)	115(239)	2.11	6.92	7	2.00	3.90	7.80
	12:30	137	25	99(210)	106[c](223)	97(207)	118(244)	1.83	6.00	8	0.80	3.75	3.00
	12:40	135	27	99(210)	108[c](226)	98(208)	124(255)	1.67	5.48	9	0.50	3.54	1.77
	1:00	121	27	98(208)	119[c](246)	97(207)	146(295)	1.49	4.89	10	0.50	3.81	1.90
	1:10	122	28	99(210)	140[c](284)	98(208)	164(327)	1.45	4.76	11	0.50	4.00	2.00
	1:30	122	29	99(210)	182[c](360)	98(208)	128[c](262)	1.40	4.59	12	0.50	3.92	1.96
	1:40	122	29	99(210)	193[c](379)	99(210)	131[c](268)	1.40	4.59	13	0.50	3.88	1.94
	1:50	122	27	99(210)	206[c](403)	100(212)	135[c](275)	1.51	4.95	14	0.50	3.92	1.96
	2:10	120	27	97(207)	213[c](415)	99(210)	150[c](302)	1.48	4.86	15	0.50	3.87	1.94
	2:20	134	32	97(207)	214[c](417)	101(214)	158[c](316)	1.39	4.56	16	0.50	3.60	1.80
	2:30	134	35	95(203)	218[c](424)	104(219)	176[c](349)	1.28	4.20	17	0.50	3.87	1.94
	2:50	135	37	93[d](199)	225[c](437)	130(266)	200[c](392)	1.21	3.97	18	0.50	4.58	2.29
	3:00	134	42	95[d](203)	226[c](439)	169(336)	218[c](424)	1.06	3.18	19	0.50	3.46	1.73
	3:10	134	46	93[d](199)	242[c](468)	115[c](239)	240[c](464)	0.97	3.18	—	—	—	—
	3:13	Power off — spot temperature check on shell — 226.7°C (440°F)											
	3:20	—	—	92[d](198)	253[c](487)	159[c](318)	255[c](491)	—	—	20	0.52	3.56	1.85
	Bottom drain							—	—	21	1.32	2.88	3.80
	Total							—	—	—	21.62	—	89.14

---

[a] Thermocouple inserted 3 inches (7.6 cm) into column.

[b] Thermocouple inserted 2 inches (5.1 cm) into column.

[c] Thermocouple inserted 1 inch (2.5 cm) into column.

[d] Thermocouple inserted 5 inches (12.7 cm) into column.

per minute, which was equivalent to 23.85 liters per minute per square meter (0.586 gallon per minute per square foot), 1024 additional grams (2.26 pounds) of volatile organic acids were added to the carbon. This was from a feed similar to that used in Run 1. The succeeding regeneration data are given in Table 28. Power connections and thermocouple configurations were the same as at the start of Run 1. At the end of 4 hours of operation the power connections were changed to the A and B position in order to heat the top foot (30.5 cm) of carbon. Shortly after, however, electrical arcing was in evidence at the top electrode.

Upon removing some of the carbon it was evident that arcing had occurred on the left side of the top electrode. The insulation on the wall of the column was repaired, the electrode was replaced and carbon was added to a depth of one inch (2.54 cm) above the electrode. The column was also insulated with 2 inches (5.08 cm) of glass wool to eliminate the condensation around the periphery of the column. It was also necessary at this time to wet the carbon with tap water to make necessary insulator adjustments. On March 8 the power connections were made over the entire 4 foot (1.2192 m) of carbon between the A and E positions, with the thermocouple configuration as follows: No. 1 at No. 1 position 4 inches (10.16 cm) into the carbon, No. 2 in the No. 2 position 2 inches (5.08 cm) into the carbon, No. 3 in the C' position 6 inches (15.24 cm) into the carbon, and No. 4 in the D' position 5 inches (12.7 cm) into the carbon. After about 20 minutes of operation there was again evidence of arcing, and so the connections were changed to the B and E position. Heating was continued for about two hours, and the power connections were again changed to cover the entire 4 foot (1.2192 m) of carbon, to the A and E positions. After about 20 minutes of operation, a strong unidentified odor was detected and power was shut off. On March 9, the following day, the power was again activated without making any changes in the configuration of the power hookup, but after about 10 minutes a strong odor was again in evidence. The insulation was removed and it was found that a spot had burned on the left side, about 1 1/2 feet (45.7 cm) down from the top of the carbon

Table 28. LOWELL UNIT — ALTERNATING CURRENT

Run 2 — Desorption or Regeneration
Filtrasorb 400 Carbon
Carbon Bed 1 ft × 4 ft (30.5 cm × 1.219 m)

Date	Time	Volts	Amps	Temperature, °C (°F) 1	2	3	4	Elec. resistance ohms/ft	ohm/meter	Sample No.	Sample size, liters	Volatile organic acids Concentration, g/l	Removed, %
2-27-73	Volatile organic acids adsorbed on carbon — 1024 grams or 2.26 lbs												
2-28-73	Power connection — B to E Thermocouple configuration: 1 — No. 1 position, 2 inches (5.1 cm) into carbon 2 — C' position, 6 inches (15.2 cm) into carbon 3 — No. 3 position, 2 inches (5.1 cm) into carbon 4 — D' position, 2 inches (5.1 cm) into carbon												
	8:22	101	97	39(102)	37(99)	35(95)	36(97)	0.35	1.15	—	—	—	—
	8:50	103	72	100(212)	96(205)	35(95)	100(212)	0.48	1.57	—	—	—	—
	8:55	Power off — repaired top gasket leak											
	9:27	Power on											
	9:40	104	63	96(205)	97(207)	—	98(208)	0.55	1.80	1	2.00	0.05	0.10
	10:00	133	52	97(207)	98(208)	—	100(212)	0.85	2.79	2	2.00	0.05	0.10
	10:20	134	34	97(207)	101(214)	—	104(219)	1.31	4.30	3	2.00	0.14	0.27
	10:40	148	27	97(207)	113(235)	—	125(257)	1.83	6.00	4	2.00	0.54	1.08
	11:10	175	25	100(212)	195(383)	—	162(324)	2.33	7.64	5	2.00	0.65	1.29
	11:40	175	22	100(212)	118ª(244)	—	206(403)	2.65	8.69	6	2.00	1.34	2.69
	12:20	175	23	101(214)	122ª(251)	—	247(478)	2.54	8.33	7	2.00	2.39	4.78
	1:00	148	40	98(208)	171ª(340)	—	155ª(311)	1.23	4.04	8	2.47	3.56	8.79
	Changed power connection from A to B												
	1:30	104	75	99(210)	—	—	—	1.39	4.56	9	1.00	5.22	5.22
	1:50	108	20	100(212)	183ª(361)	—	167ª(333)	5.40	17.72	10	1.70	9.76	16.60
	Arcing at top electrode — power off for some time												
	3:50	98	38	99ª(210)	116ª(241)	—	123ª(253)	2.58	8.46	11	2.80	3.27	9.17
	Bottom drain									12	1.30	4.04	5.26
3-1-73	Arcing had occurred on the left side of the top electrode. Repaired the wall. Replaced electrode and added carbon to a depth of 1 inch above electrode. Insulated column with 2 inchs (5.1 cm) of glass wool. Wet carbon with tap water to make insulator adjustments												
3-8-73	Power connection — A to E Thermocouple configuration: 1 — No. 1 position, 4 inches (10.2 cm) into carbon column 2 — No. 2 position, 2 inches (5.1 cm) into carbon column 3 — C' position, 6 inches (15.2 cm) into carbon column 4 — D' position, 5 inches (12.7 cm) into carbon column												
	1:13	104	41	37(99)	37(99)	37(99)	37(99)	0.63	2.07	—	—	—	—
	1:30	Power off — evidence of arcing — power connection — B to E											
	1:40	103	75	67(153)	57(135)	62(144)	72(162)	0.46	1.51	—	—	—	—
	2:30	118	39	101(214)	101(214)	102(216)	102(216)	1.01	3.31	13	3.00	0.14	0.41
	2:50	133	47	101(214)	101(214)	102(216)	105(221)	0.94	3.08	14	3.00	0.22	0.65
	3:10	134	35	101(214)	101(214)	107(225)	119(246)	1.28	4.20	15	3.00	0.46	1.38
	3:40	107	24	101(214)	106(223)	114(237)	150(302)	1.49	4.89	—	—	—	—
	Power connection — A to E												
	4:05	108	18	101(214)	102(216)	112(234)	134(273)	1.50	4.92	16	3.00	0.75	2.82
	Power off, strong odor												
3-9-73	11:40	Power on											
	11:50	106	21	67(153)	66(151)	74(165)	71(160)	1.26	4.13	—	—	—	—
	Power off, strong odor												
	Total												60.61

ªThermocouple inserted 1 inch (2.5 cm) into column.

bed. The carbon was removed and it was found that arcing had occurred in three places.

At this point in time it was decided that, although this method of heating the carbon column might still be successfully concluded, the level of work required and possible additional expenditures were too high to proceed under this particular project, and this phase of the work was terminated.

The idea was presented that perhaps the addition of a granular metal dispersed among the carbon particles would tend to prevent channeling of the electric current. In order to rapidly prove or disprove this theory, a small 2-inch diameter (5.08 cm) carbon column was set up in the laboratory. After several runs using granular aluminum, there was no evidence of improvement.

CONCLUSIONS

Attempted heating of the carbon column by the direct application of an electric current through the carbon has resulted in the following observations.

1. If direct current is used, then the anode must be at least platinum coated to prevent disintegration.
2. The packing of carbon is very important; it may even be necessary to selectively size the carbon particles.
3. A method needs to be devised to prevent localized heating and/or arcing. Proper packing would be partly helpful in preventing this.
4. Work with alternating current was hindered on this project by having only one transformer available.
5. The column should be constructed of a more heat-resistant electrical insulating material.
6. A change in design would be a requirement for successful operation. This would probably require some type of pressure

loaded electrodes to prevent loss of contact between electrodes and carbon.

SECTION VIII

INVENTION RECORD AND PUBLICATION

1. Invention record — A granular activated carbon regeneration system using alcohol as the regeneration agent and the activated carbon column as a distillation unit was conceived and reduced to practice by K. W. Baierl in the course of this research.
2. Publication — Treatment of Sulfite Evaporator Condensates for Recovery of Volatile Components, Kenneth W. Baierl, Bernard F. Lueck, and Averill J. Wiley, Tappi 56, no. 7:58-61(July, 1973).

GLOSSARY OF ABBREVIATIONS

SSCF	Steam Stripping Column Feed
SSCF	Steam Stripping Column Bottoms
SSCCO	Steam Stripping Column Condensed Overhead
FCO	Fractionation Column Overhead
FCB	Fractionation Column Bottoms
FCSC	Fractionation Column Side-cut
ACCFE	Activated Carbon Column Furfural Effluent
ACCACE	Activated Carbon Column Acetic Acid Effluent
ACCFRI	Activated Carbon Column Furfural Regeneration Inlet
ACCFRE	Activated Carbon Column Furfural Regeneration Effluent
ACCACRI	Activated Carbon Column Acetic Acid Regeneration Inlet
ACCACRE	Activated Carbon Column Acetic Acid Regeneration Effluent
FCRF	Fractionation Column Regeneration Feed (Furfural Regeneration Effluent, Acetic Acid Regeneration Effluent, or Steam Stripping Column Overhead)
FCACRB	Fractionation Column Acetic Acid Regeneration Bottoms
FCACRSC-1	Fractionation Column Acetic Acid Regeneration Side-cut No. 1
FCACRSC-2	Fractionation Column Acetic Acid Regeneration Side-cut No. 2
FCACRO	Fractionation Column Acetic Acid Regeneration Overhead
FCFRSC	Fractionation Column Furfural Regeneration Side-cut
FCFRO	Fractionation Column Furfural Regeneration Overhead
FCFRB	Fractionation Column Furfural Regeneration Bottoms

*U.S. GOVERNMENT PRINTING OFFICE: 1974 546-316/262 1-3